t Engin.
Library

TRANSACTIONS OF THE AMERICAN SOCIETY FOR METALS

MARCH, 1942

ume XXX Number 1

The TRANSACTIONS *of the*

AMERICAN SOCIETY FOR METALS

Published quarterly and Copyrighted, 1942, by the AMERICAN SOCIETY FOR METALS
7301 Euclid Avenue, Cleveland, Ohio

SUBSCRIPTIONS: (members) $2.50 per year
(non-members) $5.00 per year, $2.00 per copy
Foreign (non-members) $6.50 per year, $2.50 per copy

Entered as second class matter, November 9, 1931, at the Post Office at Cleveland, Ohio, under the Act of March 3, 1879

RAY T. BAYLESS, *Editor*

Vol. XXX March 1942 No. 1

The object of the Society shall be to promote the arts and sciences connected with either the manufacture or treatment of metals, or both.

Officers and Trustees

BRADLEY STOUGHTON, President
Lehigh University, Bethlehem, Pa.

H. J. FRENCH, Vice-President
International Nickel Co., New York

F. B. FOLEY, Treasurer
The Midvale Co., Nicetown, Philadelphia

W. H. EISENMAN, Secretary
7301 Euclid Ave., Cleveland

TRUSTEES

O. E. HARDER, Past President
Battelle Memorial Institute, Columbus, Ohio

E. L. BARTHOLOMEW
United Shoe Machinery Corp.
Beverly, Mass.

C. Y. CLAYTON
Missouri School of Mines & Metallurgy
Rolla, Mo.

N. F. TISDALE
Molybdenum Corporation of America
Pittsburgh

K. R. VAN HORN
Aluminum Company of America
Cleveland

Publication Committee

MAXWELL GENSAMER, Chairman '42
Carnegie Institute of Technology
Pittsburgh

RAY T. BAYLESS, Secretary
7301 Euclid Ave., Cleveland

Members:

J. B. Austin, New York '44
L. S. Bergen, New York '42
Walter Crafts, Buffalo '44
T. G. Digges, Washington '43
E. H. Dix, Jr., Pittsburgh '43
W. E. Jominy, Detroit '44
E. G. Mahin, Notre Dame '43
J. F. Oesterle, Milwaukee '42
Gilbert Soler, Canton-Mass. '44
Clair Upthegrove, Detroit '44
J. P. Walsted, Worcester '42
A. W. Winston, Detroit '42
L. L. Wyman, Schenectady '43
J. F. Wyzalek, New Jersey '43

East. Engineering lib.
gift E.W. Boston
3-10-44
Vol. 30, nos. 1-4
Cop 2.

Table of Contents

Page

The Martensite Thermal Arrest in Iron-Carbon Alloys and Plain Carbon Steels—
By Alden B. Greninger 1

Discussion 26

The Effect of Carbon Content and Cooling Rate on the Decomposition of Austenite During Continuous Cooling of Plain Carbon Steels—
By R. F. Thomson and C. A. Siebert 27

Discussion 43

Low Expansion Alloys for Glass-To-Metal Seals—By W. E. Kingston 47

The Effect of Strain Rate Upon the Tensile Impact Strength of Some Metals—
By E. R. Parker and C. Ferguson 68

Discussion 80

Some Properties of Sintered and Hot-Pressed Copper-Zinc Powder Compacts—
By Claus G. Goetzel 86

Discussion 117

The Precipitation Reaction in Aged Cold-Rolled Brasses: Its Effects on Hardness, Conductivity, and Tensile Properties—By R. H. Harrington and T. C. Jester 124

Discussion 142

Hardening Characteristics of an Iron-Cobalt-Tungsten Alloy—By W. P. Sykes .. 147

Discussion 164

Homogenization of Copper-Nickel Powder Alloys—
By Frederick N. Rhines and Robert A. Colton 166

Discussion 188

Study of Dimensional and Other Changes in Various Die Steels Due to Heat Treatment—By G. M. Butler, Jr. 191

Discussion 221

Hardenability Testing of Low Carbon Steels—
By R. C. Frerichs and E. S. Rowland 225

Discussion 245

Copyright 1942 by the
American Society for Metals
Cleveland, Ohio

Printed in U. S. A.

TRANSACTIONS
American Society for Metals
VOL. XXX JANUARY-DECEMBER 1942

THE MARTENSITE THERMAL ARREST IN IRON-CARBON ALLOYS AND PLAIN CARBON STEELS

By Alden B. Greninger

Abstract

A description is presented of a gas quenching apparatus for high velocity thermal analysis. Helium gas is used as the quenching medium, and time-temperature curves are recorded with the aid of a short-period torsion galvanometer and a drum camera. The temperatures of the martensite thermal arrest as a function of carbon content have been determined for both high purity iron-carbon alloys and plain carbon steel. Cooling velocities, measured at 550 degrees Cent. (1020 degrees Fahr.), up to 4000 degrees Cent. (7200 degrees Fahr.) per second were used. Time-temperature curves have also been recorded during the quenching of small specimens of steel into liquid metal baths. The results offer proof that the martensite transformation in steel cannot be suppressed by increasing cooling velocities; that is, there is no effect of cooling velocity upon the temperature of Ar".

WHEN the temperature of a small specimen of eutectoid steel is autographically recorded during rapid cooling from the austenite range, the resulting time-temperature "quenching curve" provides a record of the transformation that the austenite has undergone during cooling. If primary troostite only has formed, there will be a single prominent thermal arrest between 500 and 600 de-

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. The author, Alden B. Greninger, was formerly assistant professor of metallurgy, Graduate School of Engineering, Harvard University, Cambridge, Mass., and is now associated with the Lamp Department of the General Electric Co., Cleveland. Manuscript received June 11, 1941.

grees Cent. (930 and 1100 degrees Fahr.) and the arrest is referred to as Ar′. If the cooling velocity is sufficiently high so that only martensite forms, the single arrest is near 240 degrees Cent. (465 degrees Fahr.), is relatively weak, and is referred to as Ar″. Whenever both Ar′ and Ar″ occur on a quenching curve, the specimen contains both troostite and martensite.

The above technique of thermal analysis often has been applied in studies of the quenching of steel and has provided much of our available information relating to the transformation of austenite. In spite of the many publications that have appeared in this field, the following really important questions either have not been touched upon or have not been answered satisfactorily.

(a) Is the temperature at which martensite begins to form from austenite on cooling sensibly affected by variations in cooling velocity?

(b) Is it physically possible to increase cooling velocity to such an extent that Ar″ is completely suppressed and thus cause martensite formation to proceed at constant temperature after the specimen has reached the temperature of the quenching medium? (Certain metallurgists[1] maintain that this has been shown to happen when a small specimen of eutectoid steel is quenched into a liquid metal bath, held at, say, 250° C.

(c) What cooling velocities are attainable by quenching very small steel specimens into liquid metal baths, and how do these velocities compare with those attainable with water or brine quenching?

(d) What effect does austenizing temperature or austenite grain size have upon Ar″ temperature and the progress of the martensite transformation?

(e) How does the Ar″ temperature for a given steel, as determined from thermal quenching curves, compare with the Ar″ temperature determined microscopically by the technique of Greninger and Troiano (1)?

(f) To what extent does the Ar″ versus carbon content curve for high purity iron-carbon alloys differ from that for plain carbon steels?

This paper reports the results of an experimental study which provides satisfactory answers to the above questions.

Previous Work

According to Dejean (7),[2] the first observation of the "split

[1]See J. R. Vilella in discussion of Reference 1; also the various publications on the S-curve of austenite decomposition from the U. S. Steel Corp. Research Laboratory, particularly References 2 and 3.

[2]The figures appearing in parentheses refer to the bibliography appended to this paper.

critical point"—Ar′ and Ar″—was made by Osmond (8) in 1892, in an air hardening steel containing 6.35 per cent tungsten and 0.40 per cent carbon. In the subsequent 25-year period, several publications appeared describing the split critical points in various types of alloy steels, and in 1917 Portevin and Garvin (4), (5) first announced the experimental demonstration of Ar′ and Ar″ for plain carbon steels.[4] Their announcement was closely followed (in the same year) by those of Chevenard (6) and Dejean (7). Portevin and Garvin were also the first investigators to make use of a moderately high velocity galvanometer for the thermal analysis of steel. Chevenard used a recording differential dilatometer, and reported cooling velocities as high as 1200 degrees Cent. (2200 degrees Fahr.) per second for steel wires 0.23 millimeter diameter quenched with hydrogen gas. These early investigators succeeded in showing the existence of Ar″ for plain carbon steels, but apparently did not notice a relation between the temperature of Ar″ and carbon content.[5]

The first notable contribution to appear after the pioneer work of the French metallurgists was that of French and Klopsch (9) in 1924. Cylindrical specimens of plain carbon steels, ½ inch in diameter (with attached thermocouples), were quenched in water at different temperatures; time-temperature curves of the quenching operation were recorded with the aid of a string galvanometer. Cooling velocities (centers of specimens) ranged from about 10 to 500 degrees Cent. (18 to 900 degrees Fahr.) per second (measured at 720 degrees Cent.—1330 degrees Fahr.). French and Klopsch found that Ar″ temperatures were largely determined by the carbon contents of the steels; for specimens quenched from about 75 degrees Cent. (135 degrees Fahr.) above Ac_3, Ar″ temperatures were (± 15 degrees Cent.) independent of cooling velocity within the range of velocities studied; these evaluated Ar″ temperatures are reproduced in Fig. 1. However, for a 0.95 per cent carbon steel quenched from 875 degrees Cent. (1610 degrees Fahr.), Ar″ was found to decrease from 375 degrees Cent. (710 degrees Fahr.) to 260 degrees Cent. (500 degrees Fahr.) as the cooling velocity was increased from 160 to 260 degrees Cent. (290 to 470 degrees Fahr.) per second.

In 1930, Esser and co-workers (10) showed that time-temperature curves recorded during quenching in gaseous media were con-

[4]They proposed the terms Ar′ and Ar″, as well as the term "critical cooling velocity."

[5]Portevin and Garvin refer to "300 degrees Cent. and under," Chevenard to "200 to 300 degrees Cent.," and Dejean to "below 200 degrees Cent."

siderably more uniform than those obtained during water quenching.[6] Specimens (size varied from 4 millimeters diameter spheres to disks 2 millimeters diameter and 0.2 millimeter thick) were heated in vacuum and then quenched in nitrogen or carbon dioxide gas. Thermocouple wires welded to the specimens allowed quenching curves to be recorded with a string galvanometer. Cooling velocities (measured at 750 degrees Cent.—1380 degrees Fahr.) up to 3000 degrees Cent. (5400 degrees Fahr.) per second were attained with the smallest specimens. Tabulated results are given only for velocities up to about 1400 degrees Cent. (2500 degrees Fahr.) per second; their Ar″ curve for a cooling velocity of 1000 degrees Cent. (1800 degrees Fahr.) per second is reproduced in Fig. 1. Except for the lowest carbon contents, Esser's curves show that the Ar″ temperature for a given steel is independent of cooling velocity within the range of velocities studied.

Similar studies were reported at about the same time by Wever and Engel (12). They used fine wire specimens with two thermocouples (0.02 millimeter diameter) spot-welded to a point on the wire surface; one thermocouple was used to record the time-temperature curve during the quench and the other, inductively coupled to a separate galvanometer, recorded the first derivative of the time-temperature curve (thus a cooling velocity versus time curve) on the same photographic plate. The moving-coil galvanometers used had periods of one-fiftieth of a second. Specimens were austenized in hydrogen atmosphere and quenched in a stream of hydrogen gas. For the finest wires (ribbon, 0.03 millimeter thick) cooling velocities of 9500 degrees Cent. (17,000 degrees Fahr.) per second were attained, but the range of velocities studied for most steels extended only to about 3000 degrees Cent. (5400 degrees Fahr.) per second (measured at 900 degrees Cent.—1650 degrees Fahr.). Wever and Engel's results show Ar″ for a given steel to be independent of cooling velocity; their evaluated Ar″ temperatures are reproduced in Fig. 1. Wever and Engel are the only investigators to report martensite arrests for carbon contents below about 0.15 per cent; for example, they report a martensite arrest of 440 degrees Cent. (825 degrees Fahr.) for an alloy of electrolytic iron plus 0.037 per cent carbon.

---

[6]The anomalies present in (water) quenching curves of steel specimens that undergo no transformation during cooling had previously been described and analyzed by Pilling and Lynch (11).

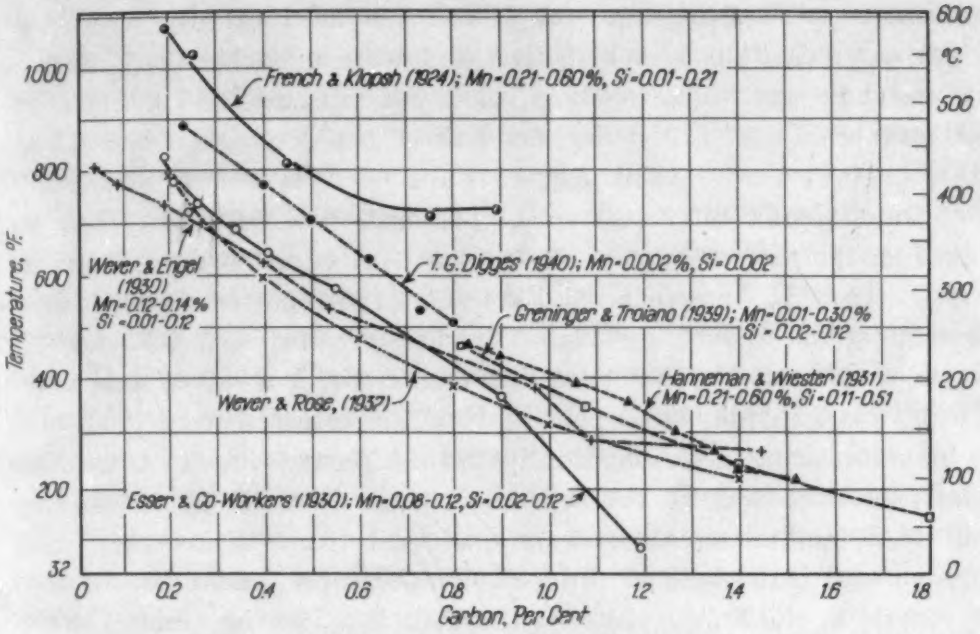


Fig. 1—Influence of Composition upon the Temperature of Ar'', as Determined by Previous Investigators. (For references, see end of text.)

Esser, Eilender, and Spenlé (13) located Ar″ temperatures by measuring magnetic induction (during gas quenching) of small specimens of high purity alloys of carbonyl iron and carbon; cooling curves were registered simultaneously to measure cooling velocities and temperatures of magnetic changes. These recordings were accomplished with the aid of two string galvanometers. Esser and co-workers concluded that Ar″ was lowered by increasing the cooling velocities; for example,[7] for an alloy containing 0.47 per cent carbon, they located Ar″ at 360 degrees Cent. (680 degrees Fahr.) for 400 degrees Cent. (720 degrees Fahr.) per second, and at 300 degrees Cent. (570 degrees Fahr.) for a cooling velocity of 1800 degrees Cent. (3250 degrees Fahr.) per second (velocities measured at 750 degrees Cent.—1380 degrees Fahr.).

Wever and Rose (14) developed a simplified scheme for recording thermal arrests during gas quenching and first applied the method to a study of Ar′ and Ar″ in relatively pure plain carbon steel. Specimens were 5 millimeters diameter, 0.5 millimeter thick; a thermocouple wire (0.3 millimeter diameter) was spot-welded to each face of the disk, and the temperature-time function was recorded, during quenching, with the aid of a moving-coil galvanometer. All

[7]The complete curves of Esser, Eilender, and Spenlé are reproduced by Epstein, Reference 16, pages 170, 171.

specimens were austenized for 2 minutes at 1000 degrees Cent. (1830 degrees Fahr.) in hydrogen and were quenched in a stream of the same gas. The cooling velocity range studied extended to 800 degrees Cent. (1450 degrees Fahr.) per second (measured at 1000 degrees Cent.—1830 degrees Fahr.). Wever and Rose state that for carbon contents above 0.4 per cent, cooling velocity has no effect on the temperature of Ar″; their Ar″ curve is reproduced in Fig. 1. In 1932, Hanemann and Wiester (15) reported a microscopic determination of Ar″ for plain carbon steels between 0.8 and 1.7 per cent carbon. At that time, Hanemann was convinced that martensite was an equilibrium phase (which he referred to as *eta*), and in his microscopic determination he did not regard time as a variable. The procedure was as follows: Specimens 5 millimeters diameter and 15-20 millimeters long were quenched from "above Ac_3" into liquid metal baths held at different temperatures, and were allowed to remain at the temperature of the bath for 5 to 10 minutes; they were then quenched in water, and examined microscopically. The upper limit of the "eta phase region" was determined by the first appearance of a few tempered martensite needles in the specimen. Hanemann and Wiester's Ar″ temperatures are reproduced in Fig. 1.

In 1939, Greninger and Troiano (1) published the results of a microscopic study of the kinetics of martensite formation in eutectoid and hypereutectoid steels. In this paper are also summarized and contrasted the prominent interpretations that have been given to the austenite-martensite transformation. The authors concluded that martensite forms from austenite only during cooling through the proper temperature range and therefore that the S-curves of Davenport and Bain (2), (3) are in error for all temperatures within the martensite range. This upper limit of the martensite range, as microscopically determined by Greninger and Troiano, is reproduced in Fig. 1. The only quenching-curve work to be published in recent years in this country is that of Digges (17), (18), (19). Digges (18) has determined the effect of carbon content on the temperature of Ar″ in high purity iron-carbon alloys; these results are reproduced in Fig. 1. Maximum and minimum values for a given composition differ by from 15 to 40 degrees Cent. (30 to 70 degrees Fahr.). No cooling velocity data are given. In this study, Digges heated specimens (0.10 inch square by 0.040 inch thick, with a 32-gage thermocouple wire spot-welded to each face of the specimen) in vacuum to 980 degrees Cent. (1800 degrees Fahr.) and quenched

them in hydrogen. Photographic time-temperature curves were obtained by means of a string galvanometer apparatus. In a later publication Digges (19) presents a curve showing the relation between Ar″ temperature and cooling velocity for a 0.8 per cent carbon alloy quenched from 775 degrees Cent. (1425 degrees Fahr.); the curve, as drawn through rather widely scattered points, shows Ar″ at 260 degrees Cent. (500 degrees Fahr.) for 220 degrees Cent. (400 degrees Fahr.) per second, and at 230 degrees Cent. (450 degrees Fahr.) for 1450 degrees Cent. (2600 degrees Fahr.) per second. Digges states that variation of austenizing temperature from 775 degrees Cent. to 980 degrees Cent. (1425 to 1800 degrees Fahr.) had no detectable effect on the temperature of Ar″ in this alloy.

Heat Evolutions for Austenite Decomposition[8]—Esser and Grass (21) have measured the heat evolved for the austenite to pearlite transformation for a 0.9 per cent carbon alloy as 21.2 calories per gram. The following measurements for the heat of the austenite to martensite transformation, referred to 721 degrees Cent. (1330 degrees Fahr.), have been determined by Esser and Bungardt (22):

0.54 per cent carbon, 13.3 calories per gram;
0.82 per cent carbon, 10.3 calories per gram;
1.40 per cent carbon, 11.0 calories per gram.

Esser and Bungardt report the following values for heat capacities for the temperature range 15 degrees Cent. to 300 degrees Cent.: austenite, 0.1333; 0.82 per cent carbon alloy, 0.1315; and 1.40 per cent carbon, 0.1348 (all in calories per gram per degree Cent.).

Discussion of Previous Work—All of the above researches have been concerned mainly with the Ar′ transformation and critical cooling velocity, and the Ar″ transformation has received small attention. All of the investigators, except Esser, Eilender, and Spenlé in their magnetometric studies, agree that the temperature of Ar″ for a given steel is affected either not at all or very little by increasing cooling velocities to the highest attainable. Yet, the various reported Ar″ temperatures for certain carbon contents differ by as much as 150 degrees Cent. (270 degrees Fahr.) (see Fig. 1), and these disparities cannot be correlated with alloy purity. Most of these publications do not contain details of procedure and results. For example, in the most recent publication from German investigators (Wever and Rose, 1937) the subject of Ar″ versus cooling velocity is covered in one sentence, and Ar″ temperatures are presented as a smooth curve with no experimental points.

[8]For measurements by other investigators, see References 21 and 22, and particularly 10.

Experimental Methods

The principal items of equipment constructed and assembled for the high-velocity thermal analysis are: a short-period galvanometer, a drum camera, and a gas quenching furnace. All of the equipment is in one room 6 feet by 9 feet, with the various items designed and arranged to enable runs to be made by one operator.

Torsion Galvanometer[9]—The galvanometer used is of the torsion, moving-coil type. The coil (resistance 24 ohms) carries a thin aluminized glass mirror 1 millimeter by 2 millimeters in area. The critical coil damping resistance is 70 ohms, and a resistance of 100 ohms is maintained in series with the thermocouple circuit; thus, the total resistance, excluding thermocouple and lead wires, is 118 ohms. The open-circuit characteristic vibrational period of the galvanometer was measured as 0.007 seconds. The following are typical deflection-time characteristics, measured photographically with the drum camera (see below) at a distance of about 50 centimeters:

Total deflection for 4 millivolts = 12 mm.
Time to reach 6 mm. = 0.003 seconds
Time to reach 11 mm. = 0.010 seconds
Time to reach 12 mm. = 0.017 seconds

The galvanometer is mounted on a small steel shelf attached to the brick wall of the building. A 4.75-volt, 8.9-ampere, galvanometer lamp[10] is used; a lens system projects a 1:1 image of the filament on the drum camera.

Drum Camera—The precision drum camera is of conventional design, modified in certain details. The drum (which carries the photographic paper[11] or film) is a machined aluminum casting 25 centimeters long and about 13 centimeters diameter supported by ball-bearings; the drum is rotated by a synchronous motor through a worm-and-spur gear drive. Change of drum speed is accomplished by the use of different drive-gear combinations; the following peripheral speeds are the most useful:

1 second = 0.5 centimeter
1 second = 2. centimeters
1 second = 10. centimeters

A detachable light-tight housing covers the drum, and contains the short-focus cylindrical lens, the shutter, and two horizontal collimat-

[9]The galvanometer was built to the writer's specifications by Mr. A. J. Lush of the Rawson Electrical Instrument Co., Cambridge, Mass.

[10]Specially constructed by General Electric Co. The filament is of type S-6.

[11]Eastman Recording Paper, Grade 697, is used for most runs.

ing slits that exclude practically all light except that reflected from the galvanometer mirror and thus eliminate the need for complete darkness during recording. To check the accuracy of the time scale on the drum, the galvanometer was employed as an alternating current vibration galvanometer using the output of a General Radio Co. 50-cycle precision fork.

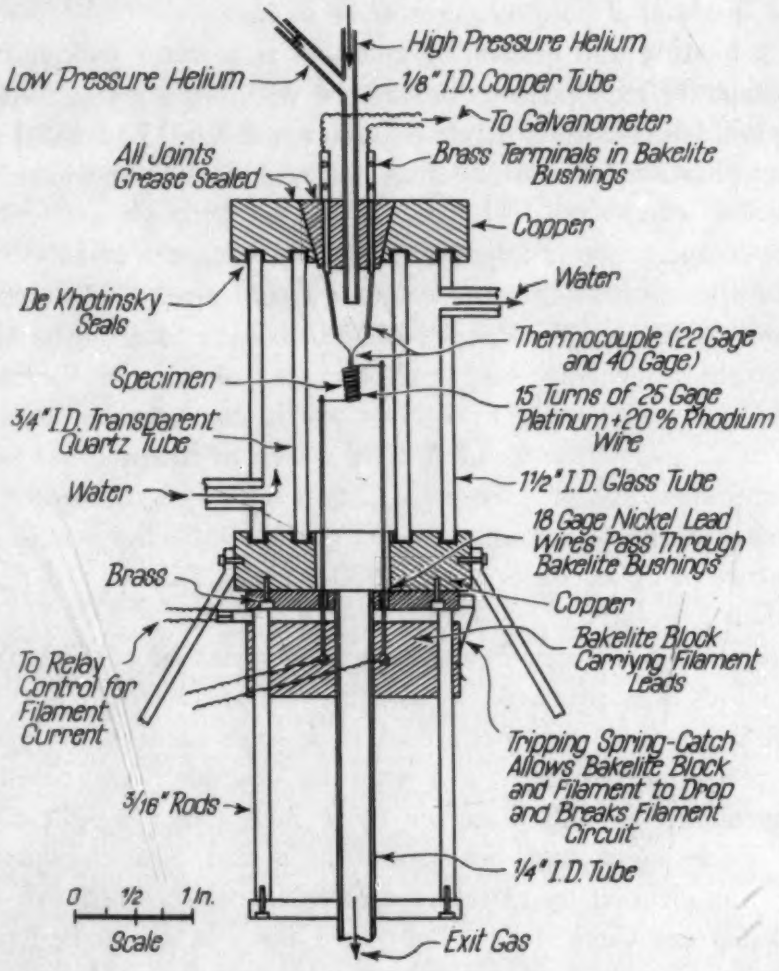


Fig. 2—Gas Quenching Apparatus.

Gas-Quenching Apparatus—The furnace used for heating and gas quenching the small specimens is illustrated in Fig. 2. The helium gas,[12] which was used for all runs, contained 98.2 per cent helium, with the balance mainly nitrogen with small traces of hydrocarbons and oxygen. The oxygen is removed by passing the gas through a small vertical quartz tube containing iron turnings (or, in some

[12]The thermal conductivity of helium is 3 per cent greater than that of hydrogen, and more than six times that of nitrogen.

runs, ferrotitanium[13]) heated to about 1000 degrees Cent. The helium flows from the tank through a pressure regulator to a spring action 2-way brass stopcock, whose two outlets are connected through calibrated needle valves to the quenching furnace; one line is used for low flow rates during austenizing, and the other for high flow rates for quenching. The highest gas pressure used in the quenching line is about 2 pounds per square inch.

The heating and quenching chamber is a water-jacketed ¾-inch inside diameter transparent quartz tube with copper end pieces. The heating coil is 0.145-inch inside diameter and has 15 turns of 25-gage platinum-plus-20-per-cent-rhodium wire, and is spot-welded to 18-gage nickel lead wires. The coil is heated through a 5-volt transformer; temperature is adjusted manually with a Variac.

The specimen used in most runs is a flat piece 0.039 inch square and about 0.010 inch thick; spot-welded to each face of the specimen is a (bright annealed) 40-gage[14] chromel or alumel thermocouple wire, $\frac{7}{16}$-inch long; these fine wires are in turn welded to 1¼-inch lengths of 22-gage thermocouple wire which fit in the brass terminals of the specimen holder (see Figs. 2 and 3). The thermocouple and lead-wire resistance amounts to 5.0 ohms; with the specimen at a temperature of 500 degrees Cent. (930 degrees Fahr.), this resistance is less than 5.4 ohms.

Alloy and Specimen Preparation—A series of high purity iron-carbon alloys was prepared by melting carbonyl iron[15] (or Wemco research iron) and sugar charcoal in a high-vacuum molybdenum-wound resistance furnace. An alumina crucible[16] was used; ingot size was about ¾-inch diameter by 1 inch long; weight about 50 grams. Each ingot was hot-forged to a rod ⅜-inch square; the forging was cleaned by grinding and was homogenized for 4 hours at 1100 degrees Cent. (2000 degrees Fahr.) in a purified nitrogen atmosphere, quenched in water, and tempered for a few minutes at 680 degrees Cent. (1250 degrees Fahr.) to produce a fine spheroidite structure. Equal amounts were then removed from all faces with a surface grinder until the bar had been reduced to 0.249-inch square.

---

[13]Professor John Chipman of Massachusetts Institute of Technology furnished the ferrotitanium used for helium purification; Professor John Wulff suggested the use of this material.

[14]For a few runs, 32-gage thermocouple wire was used instead of 40-gage.

[15]Dr. F. M. Walters, Superintendent of the Division of Physical Metallurgy, Naval Research Laboratory, kindly supplied the carbonyl iron used in this research.

[16]To Mr. T. G. McDougal and the A. C. Spark Plug Division of General Motors Corporation, I am indebted for the generous supply of excellent alumina crucibles that have been used during the past 2 years in melting iron-carbon alloys.

A ¼-inch length was cut from one end and discarded, and specimens 0.039-inch square and 0.010 to 0.020-inch thick were cut from this end of the rod with a jeweler's saw in special slotting jigs; filings for chemical analyses were taken from this same portion of the rod. Only the center 0.150-inch square section of the ¼-inch rod was used in preparing these specimens and samples. Chemical analyses of the rods were: 0.10, 0.19, 0.40, 0.62, 0.85, 1.14, and 1.36 per cent carbon.

Specimens from three different commercial plain carbon steels were prepared as follows: A 2-inch length of ½-inch square bar was cleaned and homogenized in a purified nitrogen atmosphere at 1200 degrees Cent. (2200 degrees Fahr.) for 10 to 12 hours. The bar was then reduced by milling and grinding to 0.249-inch square and specimens and a sample for chemical analysis were cut as outlined above for the iron-carbon alloys. Analyses of these plain carbon steels follow:

Steel	Per Cent Carbon	Per Cent Manganese	Per Cent Silicon	Per Cent Chromium
No. 1	0.23	0.42	0.02	...
2	0.57	0.54	0.19	0.01
3	0.84	0.62	0.23	0.04

Procedure—With the specimen and thermocouple inserted as illustrated in Fig. 2, a gas flow of 100 to 200 cubic centimeters per minute was maintained. After 5 minutes of gas flow, the coil was heated to a temperature about 50 degrees Cent. (90 degrees Fahr.) below that of the expected Ar″ for the specimen; the temperature was measured with a potentiometer and a calibration line was then exposed on the photographic paper of the drum camera. A similar calibration line was exposed for a temperature about 50 degrees Cent. (90 degrees Fahr.) above the expected Ar″. The specimen was then austenized for 5 to 10 minutes. By means of the 2-way stopcock, the helium was instantly changed from the low flow rate to the desired high flow rate, and at the same time the tripping of the spring catch (illustrated in Fig. 2) allowed the filament to drop and opened the filament circuit. The temperature-time curve during the quench was recorded by the galvanometer and drum camera. Normally, two or three quenching curves were recorded for each specimen.

To aid in the accurate location of the martensite arrest points, a series of standard cooling curves of specimens (platinum, 1.3 per

cent carbon steel, etc.) having no transformations within the temperature range studied were prepared. The appropriate standard curve was then superimposed on the curve of the alloy being studied. Ar″ could then be located with considerably more accuracy than was possible by mere inspection; this method was particularly worth while for cooling velocities higher than 1000 degrees Cent. per second.

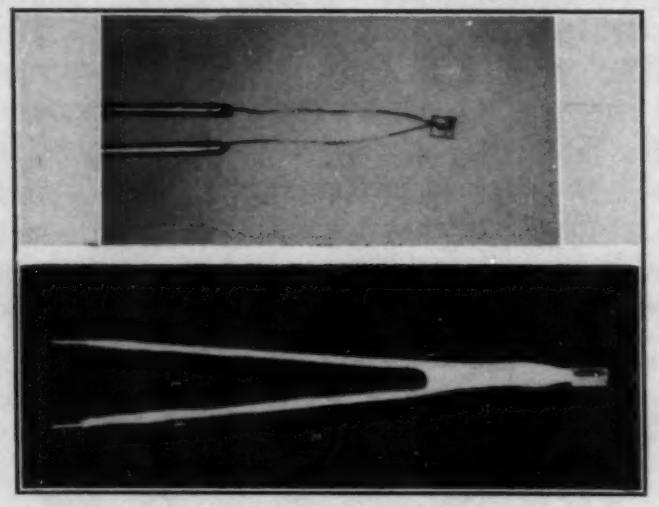


Fig. 3—(Upper) Specimen Used in Gas Quenching Apparatus. ×2.
(Lower) Specimen Used to Record Cooling Curves during Metal Bath Quenching. ×2.

Procedure Used in Quenching Specimens in Liquid Metal Baths[17]—The type of specimen used for these studies is illustrated in Fig. 3b. The ends of 32-gage chromel and alumel thermocouple wires (1 inch long) are welded between two specimens of size 0.040 by 0.020-inch by about 0.125-inch. The assembly then consists effectively of a solid specimen 0.040-inch square and ⅛-inch long[18] with a thermocouple welded to the center of one end. The thermocouple wires and this end of the specimen are covered with a layer of "Insalute" cement (liquid porcelain), and the free ends of these wires are spot-welded to 12-inch lengths of 22-gage thermocouple wire supported in a 2-hole insulator. The specimen is then heated in a vertical tube furnace in a purified nitrogen atmosphere, and

[17]Mr. Haim Chiswik helped with these metal bath quenching experiments as well as in the preparation of some of the iron-carbon alloys.

[18]This is the size of the sliver specimen used in the writer's laboratory during the past few years in studies of subcritical decomposition of austenite. The size may be considered a reasonable minimum for heat treatment and microstructure studies.

quenched in a liquid metal bath; the specimens are immersed in the bath only about ½-inch so that the Insalute cement will protect the thermocouple from the short circuit that would otherwise occur. The time-temperature curve of the quenching operation is recorded with the galvanometer and drum camera described above.

Results

The results summarized in Table I are for austenizing temperatures 70 to 90 degrees Cent. (125 to 160 degrees Fahr.) above A_3 or A_{cm}, for times varying from 5 to 10 minutes. (The effect of departure from these standard conditions is described below.) Average results are shown graphically in Fig. 4, wherein the circle diameter

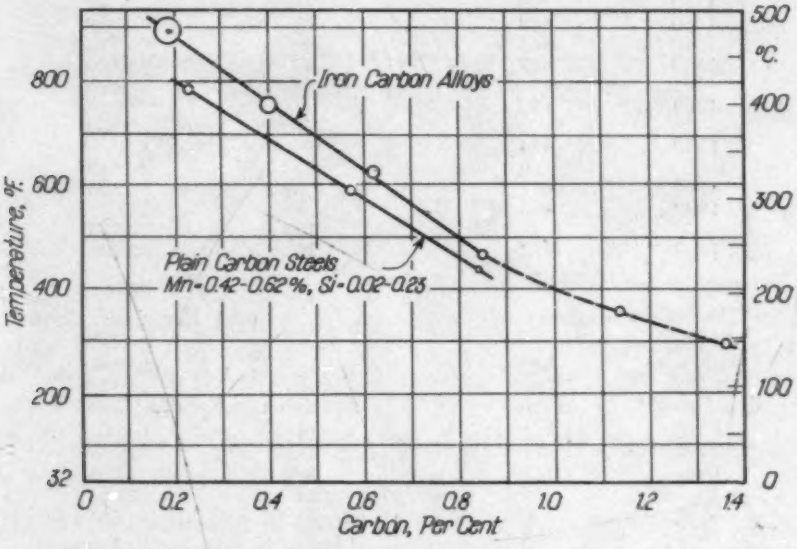


Fig. 4—Influence of Composition upon the Temperature of Ar″, for Specimens Austenized 5 to 10 Minutes at 70 to 90 Degrees Cent. above A_3 or A_{cm}. Temperatures for the hypereutectoid compositions were determined microscopically only.

represents the probable uncertainty in the location of each point. Photographic reproductions of typical quenching curves appear in Figs. 5, 6, 7, and 8.

Only Ar_3 was detected for the 0.10 per cent carbon alloy. The least satisfactory Ar″ point located is for the 0.19 per cent carbon alloy. Note that the discrepancies are mainly among different specimens and are not large for different measurements on the same specimen. The ingot was probably not entirely homogeneous, though two chemical analyses both gave 0.19 per cent carbon. The results for the plain carbon steels show more uniformity than those for the

Table I
Ar″ Temperatures for Iron-Carbon Alloys

0.19 Per Cent Carbon			0.40 Per Cent Carbon		
Specimen*	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.	Specimen	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.
1a	1550	480	1a	2700	398
1b	1350	480	1b	1550	404
1c	1350	484	1c	2700	398
1d	900	487	1d	2400	398
1e	750	484			
			2a	1500	405
2a	3000	471	2b	2100	399
2b	3000	479			
2c	3100	471	3a†	1000	395
2d	1700	485	3b†	1700	393
			3c†‡	450	397
3a	3000	470	3d†	1700	391
3b	3000	470	3e†‡	330	401
4a†	1560	464	4a	1400	394
4b†	1560	464	4b	2700	391
4c†	1560	461	4c	750	397
4d†	1560	467	4d	2400	395
			4e	600	403
5a	1200	492			
			5a	1500	396
6a	1250	494			
			6a	1250	399
7a	1700	491	6b	1100	401
7b	1800	496			
			7a	1300	405
8a	1800	492	7b	1300	404

0.62 Per Cent Carbon			0.85 Per Cent Carbon		
Specimen	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.	Specimen	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.
1a	1550	324	1a	1150	239
1b	2400	321	1b	2000	237
1c	1600	323	1c	700	241
			1d	2000	239
2a	2350	325	1e	620	242
2b	1550	332			
2c‡	410	336	2a	1250	236
2d	2700	329	2b	550	243
			2c	2200	235
3a‡	510	332	2d	1250	238
3b	2700	323			
3c	2500	325	3a	1500	237
3d	2500	327	3b	1450	238
4a	1400	323	4a	1250	245
			4b	1250	244
5a	1450	330			
5b	1300	329	5a	1750	246
6a	1200	326	6a	300	243
6b	1300	325	6b‡	175	243
			7a	350	240
			7b‡	270	243

* 1a, 1b, 1c, etc., refer to quenchings of the same specimen.
† 32-gage wire instead of 40-gage.
‡Ar′ also present on curve.
**In degrees Cent. per second.

Table II
Ar″ Temperatures for Plain Carbon Steels

0.23 Per Cent Carbon			0.84 Per Cent Carbon		
Specimen	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.	Specimen	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.
1a	1300	417	1a	250	225
1b	1200	419			
1c*	450	419	2a	220	226
2a	2600	410	3a	160	221
2b*	500	414	3b*	100	221
2c	2000	412	3c	160	226
2d	1400	414			
			4a	2000	222
3a	2200	411	4b	1400	219
3b*	470	415	4c	1700	223
3c	2100	409	4d	1400	224
3d	1450	414			
			5a	3600	220
			5b	3000	218
			6a	4000	220
			7a	3700	216
			8a	3500	215

0.57 Per Cent Carbon		
Specimen	Cooling Velocity at 550 deg. Cent.**	Ar″ Deg. Cent.
1a	2000	309
1b	500	307
2a	350	306
2b*	140	312
3a	1580	300
4a	1400	302

* Ar′ also present on curve.
**In degrees Cent. per second.

iron-carbon alloys, probably because of better chemical homogeneity in the former.

High Austenizing Temperatures—Previous microscopic studies had established (20) that austenizing temperature has a measurable effect on Ar″ and a marked effect on the amount of martensite formed per degree of temperature drop below Ar″. These conclusions are in complete agreement with the results of the present study. An increase in the austenizing temperature for the eutectoid alloys from 800 degrees Cent. (1470 degrees Fahr.) to 1000 degrees Cent. (1830 degrees Fahr.) causes Ar″ to be much less pronounced, and the cooling curve resembles that of the 1.14 per cent carbon steel (which was austenized at 1000 degrees Cent. (1830 degrees Fahr.) of Fig. 5. Ar″ is raised about 15 degrees Cent. (30 degrees Fahr.) and obviously less martensite is formed per degree drop in temperature below Ar″; this results in a gradual instead of an abrupt arrest.

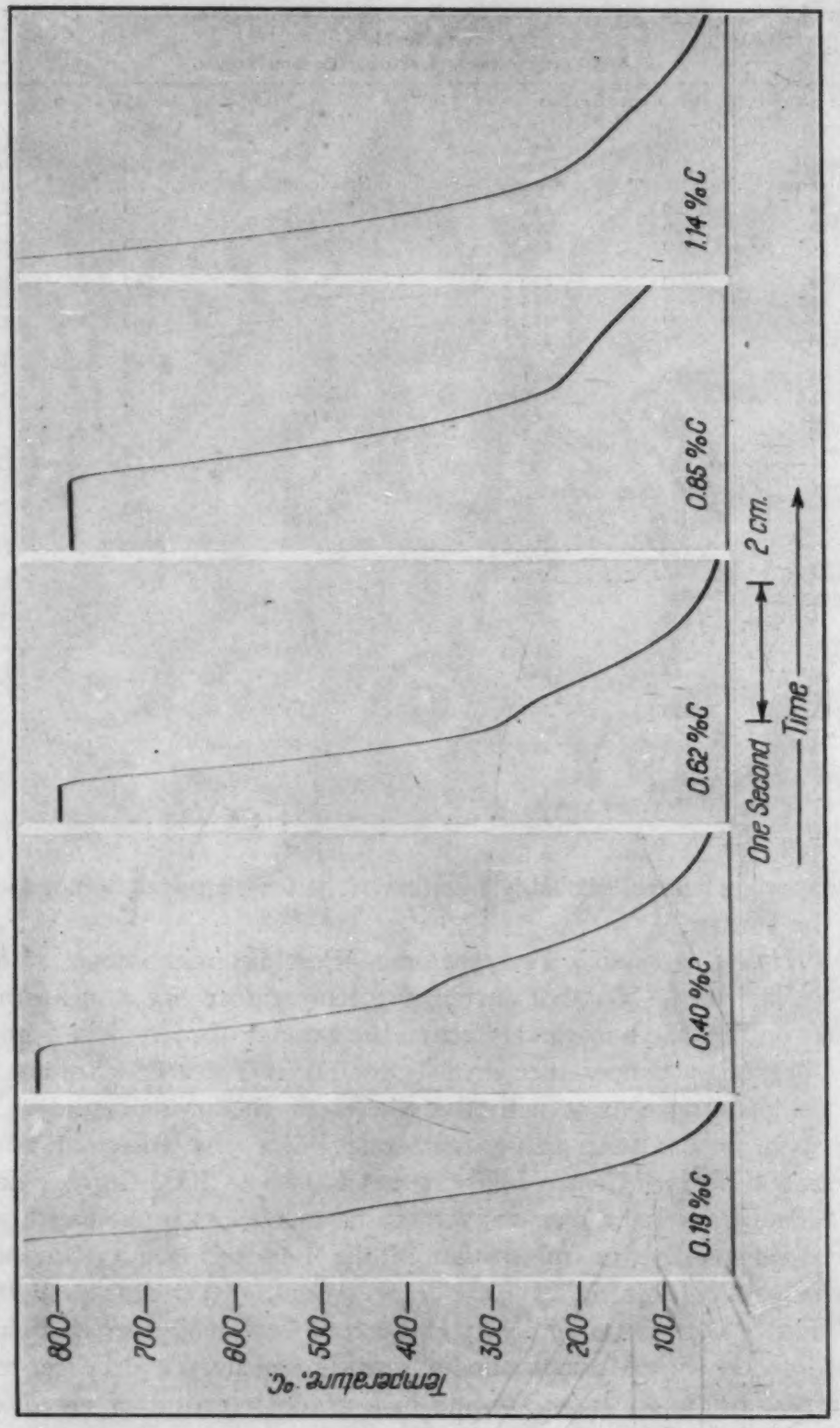


Fig. 5—Typical Gas Quenching Curves for High Purity Iron-Carbon Alloys. Cooling velocities, at 550 degrees Cent., from left to right: 1700, 1300, 1300, 1050, and 1200 degrees Cent. per second, respectively.

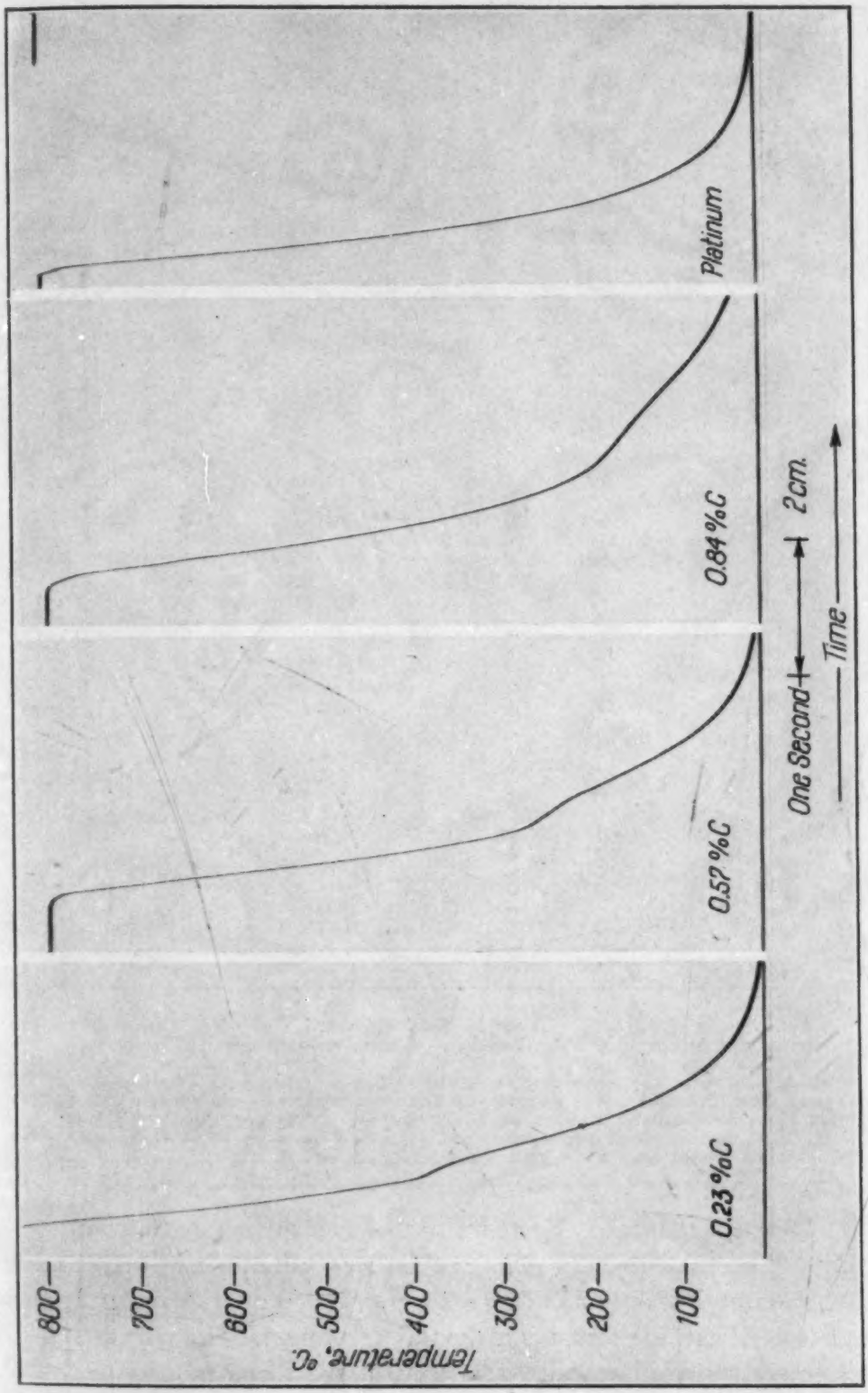


Fig. 6—Typical Gas Quenching Curves for Plain Carbon Steels (and Platinum). Cooling velocities, at 550 degrees Cent., from left to right: 1150, 1400, 1100, and 1600 degrees Cent. per second, respectively.

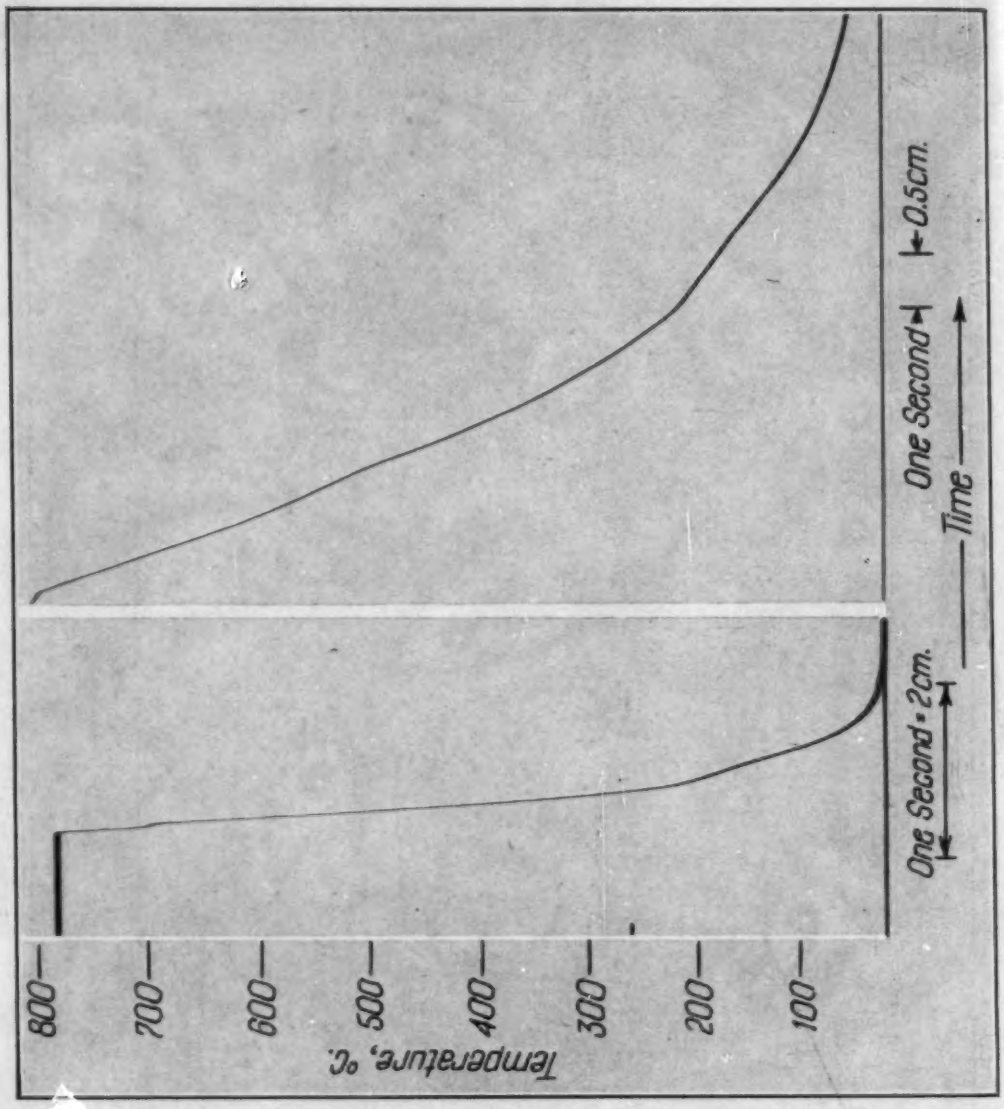


Fig. 7—Gas Quenching Curves of Eutectoid Steel (0.84 Per Cent Carbon) for Maximum and Minimum Cooling Velocities. Cooling velocities, at 550 degrees Cent., of (a) = 3600 degrees Cent. per second, (b) = 100 degrees Cent. per second. Note weak Ar′ on curve (b), extending from 610 to 520 degrees Cent. The anomaly at 700 degrees Cent. in curve (a) is undoubtedly due to turbulence in the gas quenching chamber. This effect usually appears on gas quenching curves for velocities greater than about 2500 degrees Cent. per second, and for extensive work at these high velocities the chamber would have to be redesigned.

Low Austenizing Temperature—Five quenching curves were recorded of the eutectoid plain carbon steel after it had been austenized 5 minutes at only 732 degrees Cent. (1350 degrees Fahr.); some undissolved carbide remains after this treatment. The curves showed extremely sharp martensite arrests, and the temperatures were 220, 222, 221, 223, and 225 degrees Cent. The high purity eutectoid alloy,

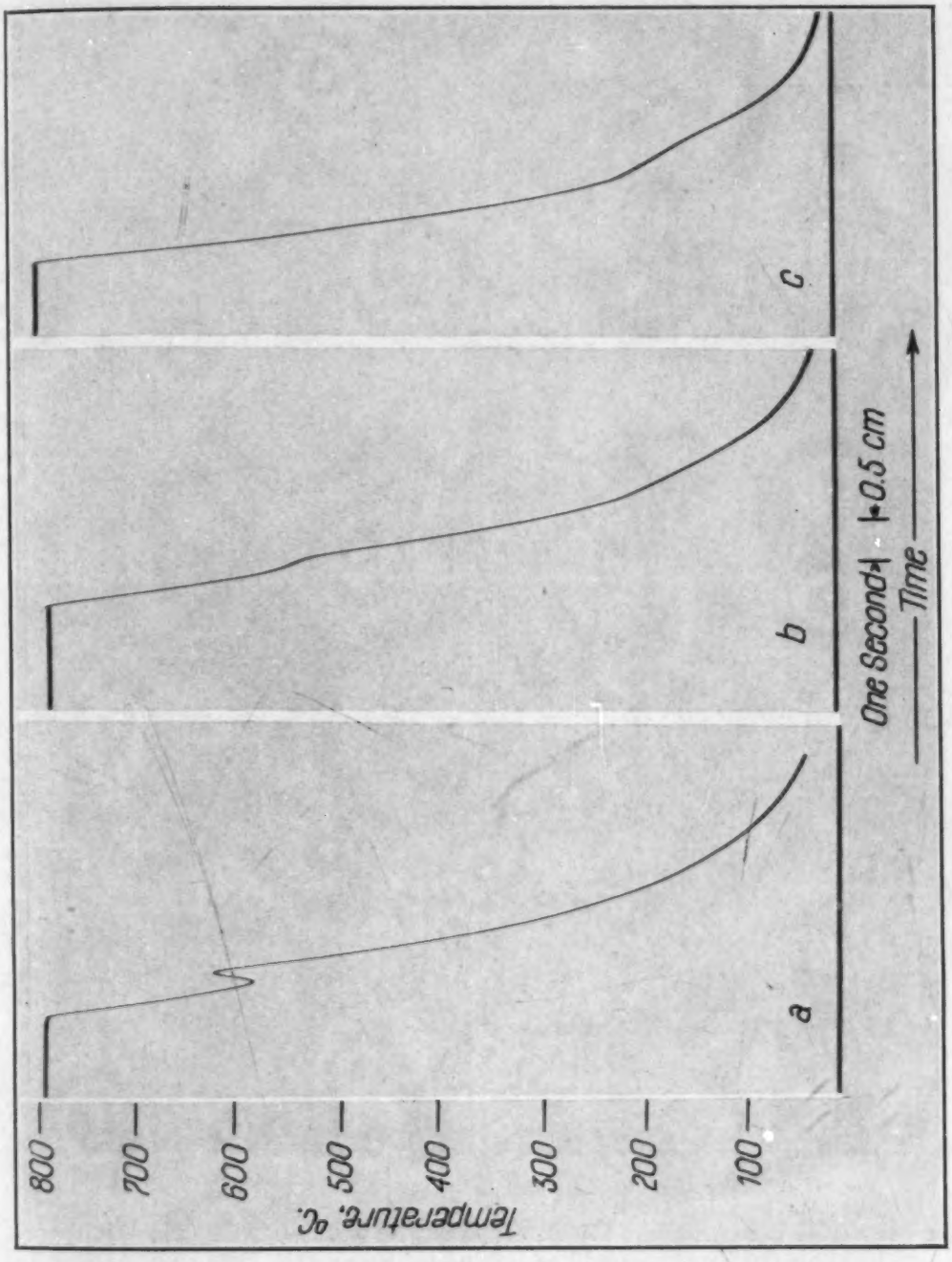


Fig. 8—Gas Quenching Curves Illustrating Comparative Prominence of Ar′ and Ar″ of the Eutectoid Iron-Carbon Alloy (0.85 Per Cent Carbon). Cooling velocities in degrees Cent. per second at 550 degrees Cent. and arrests are: (a) 150 Ar′ only; (b) 175, Ar′ and Ar″; (c) 300, Ar″ and very weak Ar′. Curve (a) represents maximum prominence of Ar′ that results when entire specimen transforms to troostite in a small fraction of a second.

similarly treated, gave curves with equally sharp arrests at temperatures of 236, 233, 233, and 234 degrees Cent.

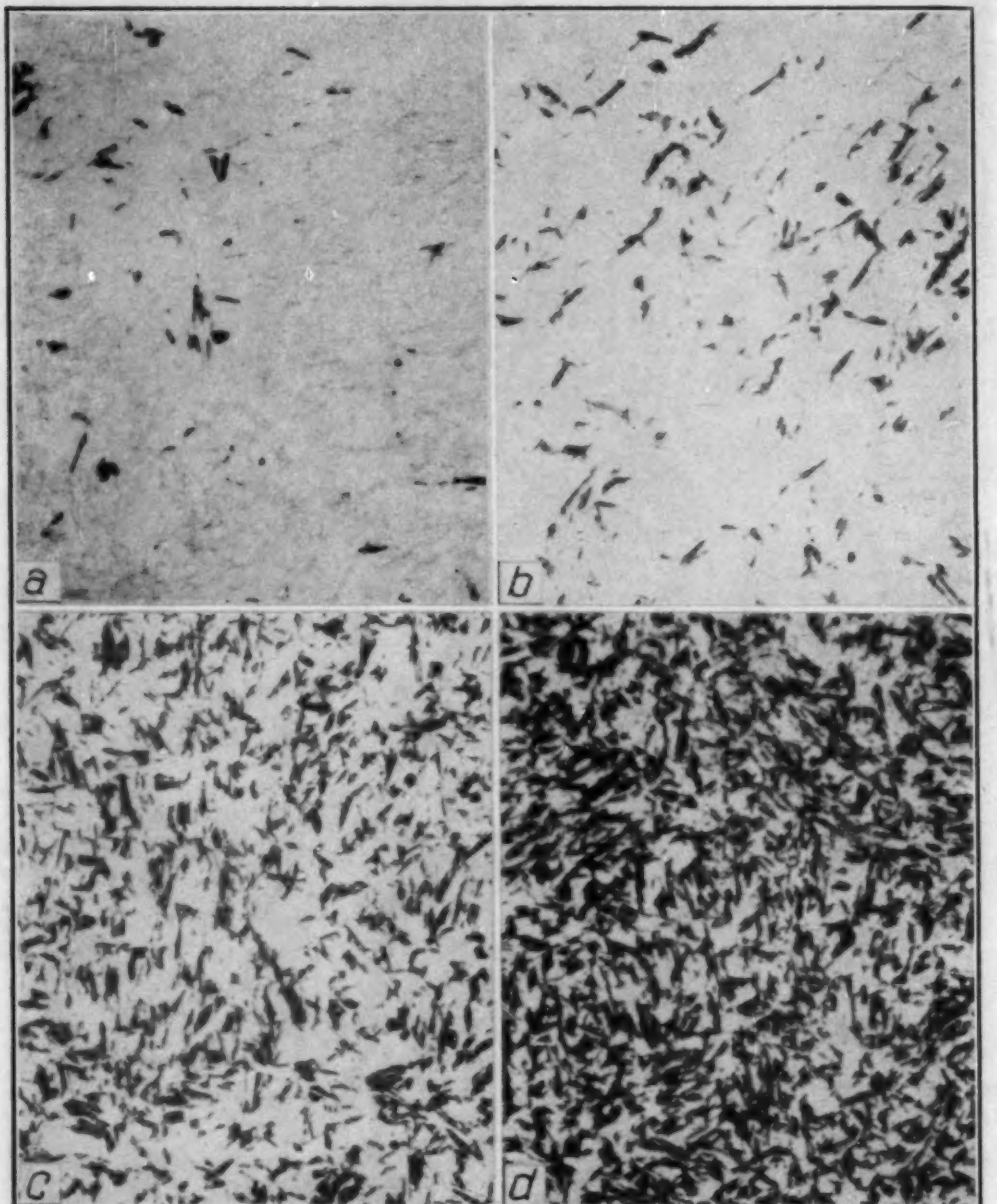


Fig. 9—0.57 Per Cent Carbon Steel Quenched to Various Temperatures and Held in Quenching Bath for 2 seconds. × 500. See text for details.
Fig. 9a—300 degrees Cent.
Fig. 9b—292 degrees Cent.
Fig. 9c—283 degrees Cent.
Fig. 9d—272 degrees Cent.

Comparison of Ar″ Determined Thermally and Microscopically —The upper limit of the martensite range was determined microscopically by the technique of Greninger and Troiano (1) for the 0.62 and 0.85 per cent carbon iron-carbon alloys[19] and for the 0.57

[19]For hypereutectoid alloys, Ar″ was determined only by the microscopic method.

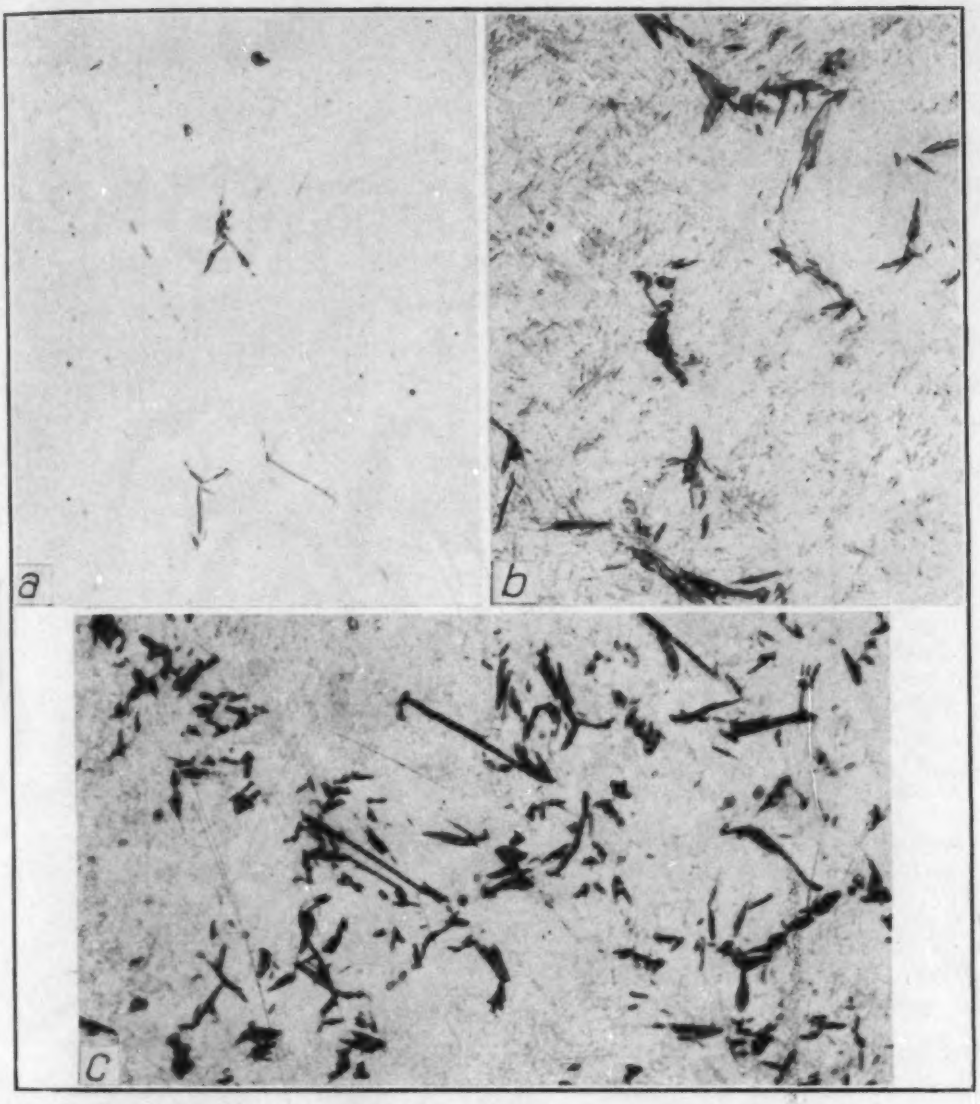


Fig. 10—0.84 Per Cent Carbon Steel Quenched to Various Temperatures and Held in Quenching Bath for 2 Seconds. × 500. See text for details.
Fig. 10a—224 degrees Cent.
Fig. 10b—221 degrees Cent.
Fig. 10c—215 degrees Cent.

and 0.84 per cent carbon commercial steels. The results obtained for the plain carbon steels are shown in Figs. 9 and 10. The specimens used were 0.040 inch square and ⅛ inch long; they were heated (austenizing temperature was 810 degrees Cent. (1490 degrees Fahr.) in purified nitrogen atmosphere and quenched in a liquid Wood's metal bath at different temperatures. After remaining in the quenching bath for 2 seconds, they were transferred rapidly to a second Wood's metal bath [this tempering bath was at 250 degrees Cent.

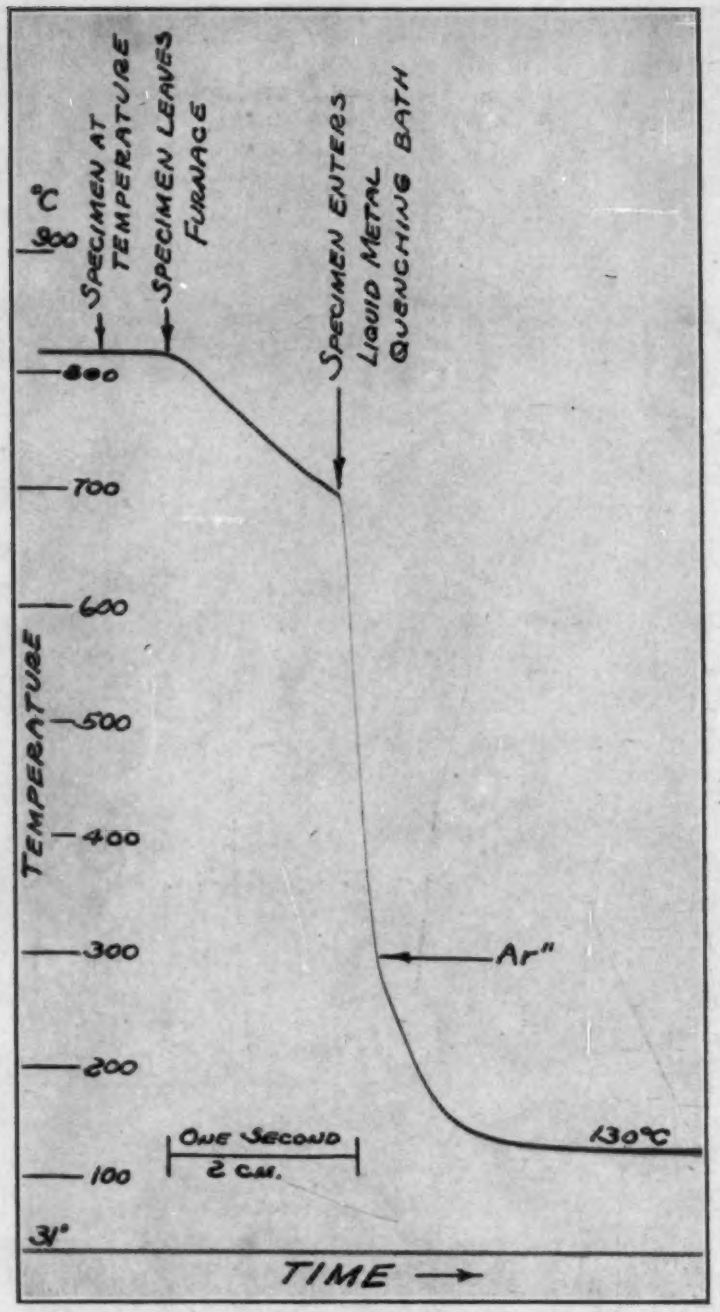


Fig. 11—Cooling Curve for 0.57 Per Cent Carbon Steel Quenched into Liquid Metal Bath.

(480 degrees Fahr.)] for the eutectoid alloy and at 320 degrees Cent. (600 degrees Fahr.) for the hypoeutectoid alloy, where they remained for 2 or 3 seconds, and were then quenched in 5 per cent NaOH solution. As may be seen by comparing the results shown

in Figs. 9 and 10 with those shown in Fig. 4, the microscopic results for Ar″ differ by less than 5 degrees Cent. (9 degrees Fahr.) from the averages of Ar″ temperatures measured with thermal quenching curves.

Time-Temperature Curves for Metal Bath Quenching—Quenching curves were recorded for both the 0.57 and the 0.84 per cent carbon steels during the quenching of specimens in liquid metal baths; the type of specimen used and the procedure followed has been described above. Four specimens of each steel were used; austenizing temperatures were about 75 degrees Cent. (130 degrees Fahr.) above A_3. Normally each specimen was quenched into the metal bath and was then reheated and used to measure cooling velocities in water or brine quenching. The following cooling velocities measured at 550 degrees Cent. (1020 degrees Fahr.) were recorded:

	Temperature		Cooling Velocity	
Quenching Medium	Deg. Cent.	Deg. Fahr.	Deg. Cent. per Second	Deg. Fahr. per Second
Wood's metal	260	500	1500	2700
Wood's metal	130	265	2700	4900
Wood's metal	108	225	3200 to 4000	5800 to 7200
Water	20	68	9000*	16,000*
5 per cent NaOH	20	68	12,000*	22,000*

One of the quenching curves is reproduced in Fig. 11, taken from a specimen of 0.57 per cent carbon steel quenched into a metal bath at 130 degrees Cent. (265 degrees Fahr.). Note that Ar″ is clearly revealed; in other words, it is certain that martensite began to form when the temperature of the specimen had been lowered to about 300 degrees Cent. (570 degrees Fahr.) and that martensite continued to form as the specimen temperature dropped; by the time (1.1 second) the specimen had reached bath temperature, it contained probably at least 80 per cent martensite.

Discussion

The Ar″ curve for high purity iron-carbon alloys (Fig. 4) from this research is in close agreement with the curve of Digges (reproduced in Fig. 1). The curves, within the range of carbon contents covered by Digges, are both straight lines, have almost identical

[20] ± 20 per cent.

slopes, and differ in position by not more than 10 degrees Cent. (18 degrees Fahr.). This difference is probably mostly due to the fact that Digges used considerably higher austenizing temperatures; he does not report cooling velocities used.

The only Ar″ curve for hypoeutectoid plain carbon steels previously published is that of French and Klopsch (see Fig. 1); undoubtedly the temperatures represented by them are much too high. Likewise the temperatures reported for the relatively pure steels by the German investigators are undoubtedly too low. This is understandable in the case of Wever and Rose (14); their recording technique would almost certainly yield low values.

There appears to be no real effect of cooling velocity upon the temperature of Ar″ in either the high purity alloys or plain carbon steel.[21] For the eutectoid steel, the range of velocities covered extends from near the critical cooling rate (about 100 degrees Cent. (180 degrees Fahr.) per second to 4000 degrees Cent. (7200 degrees Fahr.) per second. An even more extensive range of velocities is included when we compare Ar″ temperatures as determined by the microscopic technique of Greninger and Troiano with Ar″ temperatures determined from quenching curves. When a specimen of 0.84 per cent carbon steel is quenched into a metal bath held at 221 degrees Cent. (430 degrees Fahr.), its cooling velocity *at* Ar″ is very close to zero; whereas, a specimen gas-quenched at the rate of 4000 degrees Cent. (7200 degrees Fahr.) per second at 550 degrees Cent. has a cooling velocity when a few degrees above Ar″ of about 1400 degrees Cent. (2500 degrees Fahr.) per second. Yet these two experiments yield results for the Ar″ temperature for this steel that differ by no more than the experimental error of the latter.

Faced with all of the above facts, one can only conclude that the effect of cooling velocity upon the Ar″ temperature in steel is insignificant.

Acknowledgment

Grants from the Milton Fund and the Committee on Resources in the Physical Sciences of Harvard University helped to defray the expense of this investigation.

[21] In this respect, and in this only, the martensite transformation resembles the A_2 transformation and is completely unlike the A_3 and A_1 transformations.

Bibliography

1. A. B. Greninger and A. R. Troiano "Kinetics of the Austenite to Martensite Transformation in Steel," TRANSACTIONS, American Society for Metals, Vol. 28, 1940, p. 537-574.
2. E. S. Davenport and E. C. Bain, "The Transformation of Austenite at Constant Subcritical Temperatures," *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 90, 1930, p. 117-144.
3. Contribution from Research Laboratory, United States Steel Corp., "The Process and Result of Austenite Transformation at Constant Temperature," *Metals and Alloys,* Vol. 8, 1937, p. 22-24.
4. A. M. Portevin and M. Garvin, "Influence de la vitesse de refroidissement sur la température de transformation et la structure des aciers au carbone," *Comptes rendus,* Academie des Sciences, Vol. 164, 1917, p. 885; also, *Revue de Métallurgie,* Vol. 14, 1917, p. 607-609.
5. A. M. Portevin and M. Garvin, "The Experimental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels," *Journal,* Iron and Steel Institute, Vol. 99, 1919, p. 469-559.
6. P. Chevenard, "Méchanisme de la trempe des aciers au carbone," *Comptes rendus,* Academie des Sciences, Vol. 165, 1917, p. 59-62; also, *Revue de Métallurgie,* Vol. 16, 1919, p. 17-79.
7. P. Dejean, "Sur la formation de la troostite et de la martensite," *Comptes rendus,* Academie des Sciences, Vol. 165, 1917, p. 182-185; also, *Revue de Métallurgie,* Vol. 14, 1917, p. 641-675.
8. F. Osmond, "Sur le méthode de refroidissement considérée comme méthode de l'Essai des Métaux," *Commission des Méthodes d'Essais, Première session,* Vol. 2, 1892, p. 43.
9. H. J. French and O. Z. Klopsch, "Quenching Diagrams for Carbon Steels in Relation to some Quenching Media for Heat Treatment," TRANSACTIONS, American Society for Steel Treating, Vol. 6, 1924, p. 251-293.
10. H. Esser, W. Eilender, K. Riedel, and E. Spenlé, "Ueber die Stahlhärtung," *Archiv für das Eisenhüttenwesen,* Vol. 4, 1930, p. 113-144.
11. N. B. Pilling and T. D. Lynch, "Cooling Properties of Technical Quenching Liquids," *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 62, 1920, p. 665-685.
12. F. Wever and N. Engel, "Ueber den Einfluss der Abkühlungsgeschwindigkeit auf die Temperatur der Umwandlungen, das Gefüge und den Feinbau der Eisen-Kohlenstoff-Legierungen," *Mitteilungen,* Kaiser Wilhelm Institut für Eisenforschung, Vol. 12, 1930, p. 93-114.
13. H. Esser, W. Eilender, and E. Spenlé, "Das Härtungsschaubild der Eisen-Kohlenstoff-Legierungen," *Archiv für das Eisenhüttenwesen,* Vol. 6, 1933, p. 389-393.
14. F. Wever and A. Rose, "Ueber den Einfluss der Abkühlungsgeschwindigkeit auf die Umwandlungen der Stähle," *Mitteilungen,* Kaiser Wilhelm Institute für Eisenforschung, Vol. 19, 1937, p. 289-298.
15. H. Hanemann and H. J. Wiester, "Die Martensitkristallisation in hoch Kohlenstoffhaltigen Stählen," *Archiv für das Eisenhüttenwesen,* Vol. 5, 1932, p. 377-382.
16. S. Epstein, "The Alloys of Iron and Carbon," Vol. 1, "Constitution." 1936. McGraw-Hill Book Co., New York City.
17. T. G. Digges, "Effect of Carbon on the Critical Cooling Rate of High Purity Iron-Carbon Alloys and Plain Carbon Steels," *Journal of Research,* National Bureau of Standards, Vol. 20, 1938, p. 571-587.

18. T. G. Digges, "Transformation of Austenite on Quenching High Puriyt Iron-Carbon Alloys," TRANSACTIONS, American Society for Metals, Vol. 28, 1940, p. 575-607.

19. T. G. Digges, "Influence of Austenite Grain Size on the Critical Cooling Rate of High Purity Iron-Carbon Alloys," American Society for Metals, 1940 *Preprint* No. 10.

20. Unpublished research by W. D. Riddle, Jr., formerly graduate student, Harvard University.

21. H. Esser and W. Grass, "Die Wärmetönung der Austenit-Perlit-Umwandlung," *Stahl und Eisen*, Vol. 53, 1933, p. 92.

22. H. Esser and W. Bungardt, "Die Wärmetönung der Austenit-Martensit-Umwandlung," *Archiv für das Eisenhüttenwesen*, Vol. 7, 1934, p. 533-536.

DISCUSSION

MAXWELL GENSAMER:[23] I should like to ask if the author checked the carbon content by any subsequent treatment of their specimens, say microscopically; we have usually gotten some decarburization in helium.

Author's Reply

The use of commercial helium in heat treatment of steel will result in decarburization, and it was necessary to remove the oxygen present in the helium before it passes into the heating chamber of the quenching apparatus. As stated in the paper, this was done by passing the helium through a furnace containing iron turnings or ferrotitanium, heated to 1000 degrees Cent. This treatment evidently resulted in the removal of all of the oxygen. We observed no decarburization whatsoever after using purified helium.

[23]Associate professor of metallurgy, Carnegie Institute of Technology, Metals Research Laboratory, Pittsburgh.

THE EFFECT OF CARBON CONTENT AND COOLING RATE ON THE DECOMPOSITION OF AUSTENITE DURING CONTINUOUS COOLING OF PLAIN CARBON STEELS

By R. F. Thomson and C. A. Siebert

Abstract

The decomposition of austenite during quenching was studied in a series of plain carbon steels by investigating the effects of the variables, carbon content, grain size, and cooling rate.

Quantitative data are presented for the variations in microstructure in the partially hardened zone of a quenched bar as a function of cooling rate and hardness.

THE problem of the decomposition of austenite has received much attention in the literature in the last ten years. A great deal has been done on the isothermal decomposition of austenite (1)[1], and other investigators (2) have used a constant rate of cooling to follow the course of the decomposition. There is much quantitative data for the continuous cooling process with changing rate of cooling, but here most of the interest has been directed to either the fully hardened areas (less than 5 per cent fine pearlite) or to the zone of 50 per cent martensite and 50 per cent fine pearlite. The precipitation of ferrite in the hypoeutectoid steels has received similar attention during isothermal precipitation (3) and during continuous cooling (4). The authors found little quantitative data for the zone where the microstructure varies from 100 per cent martensite to 100 per cent fine pearlite plus proeutectoid ferrite, which is formed during the continuous cooling of steel of suitable section sizes from the austenitic range to room temperature. Data covering the above zone should be useful in the quantitative study of hardenability.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

This paper is based on a dissertation presented by Robert F. Thomson to the Faculty of the Horace H. Rackham School of Graduate Studies at the University of Michigan in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. Of the authors, R. F. Thomson is in the Aircraft Division, Chrysler Corp., Detroit, and C. A. Siebert is assistant professor of metallurgical engineering, University of Michigan, Ann Arbor, Mich. Manuscript received June 21, 1941.

This investigation deals with the effects of carbon content, austenitic grain size, and cooling rate on the varying proportions of martensite, fine pearlite, and proeutectoid ferrite produced during continuous cooling. For convenience throughout this paper, the term *ferrite* will be used to represent proeutectoid ferrite, that is, the ferrite not associated with the pearlite.

Procedure

Steels Investigated—The steels used in this investigation were open-hearth steels of the analyses shown in Table I.

Table I
Analyses of Steels Used in This Investigation

Steel No.	Per Cent C	Mn	P	S	Si	Ni	Cr	Ladle Deoxidation	McQuaid-Ehn Grain Size Billet Products
Series A									
5	0.23	0.81	0.019	0.025	0.22	0.06	0.06	Si + Al	6/7
8	0.39	0.79	0.017	0.032	0.24	0.08	0.04	Si + Al	5/7
7	0.61	0.80	0.018	0.022	0.25	0.05	0.03	Si + Al	6/7
Series B									
16	0.41	0.79	0.015	0.026	0.20	0.07	0.07	Si + Mn	1/2
17	0.54	0.81						Si + Mn	1/2
18	0.68	0.80						Si + Mn	1/2

The steels in Series A came from different heats. The bars as received were 1¼-inch round bars which had been forged from billets taken from the central portion of the ingots. The steels in Series B came from different ingots of the same heat having the basic composition of steel No. 16. Crushed carbon electrodes were added to two ingots to produce varying carbon contents for steels Nos. 17 and 18. The billets in Series B were forged to 1½-inch round bars.

All bars were given a preliminary heat treatment by air cooling from the temperatures shown in Table II. This table also shows the hardening temperatures used in this investigation and the austenitic grain size produced at the hardening temperature.

Table II
Heat Treating Temperatures Used in This Investigation

Steel No.	Normalizing Temperature Degrees Fahr.	Hardening Temperature Degrees Fahr.	Austenitic Grain Size Produced (A.S.T.M.)
5	1700	1650	8
8	1615	1600	8
7	1580	1520	8
16	1620	1550	Duplexed 2-7
17	1585	1540	Duplexed 2-7
18	1540	1520	Duplexed 2-7

Experimental Procedure

Sample Preparation—The end quench test (5) was used in this investigation to provide the variation in cooling characteristics required. The samples were modified, as shown in Fig. 1, to obtain the range of cooling characteristics for any given steel, which would produce a microstructure varying from 100 per cent martensite at

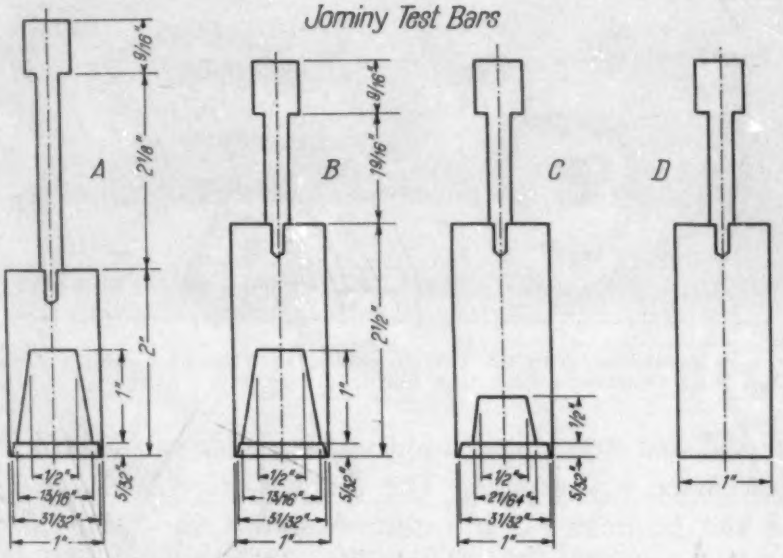


Fig. 1—End Quench Test Bars. Sample Dimensions.

the water-cooled end to a structure consisting of pearlite and appreciable amounts of ferrite at the end remote from the water spray. On each sample, two longitudinal flat surfaces were ground 30 degrees apart, to a depth of 0.012 inches measured on the diameter of the sample. On one of these flat surfaces, a No. 22-gage chromel-alumel thermocouple was welded. The wires were individually resistance welded to the flat surface at the same distance from the water-quenched end, but were separated from each other by about $\frac{1}{32}$ of an inch. The wires were insulated from each other by threading the wires through $\frac{1}{8}$-inch diameter, two-holed porcelain insulators. The thermocouple wires protruded from the insulator as shown in Fig. 2.

Heating and Cooling Samples—For measuring temperatures during heating and quenching, the thermocouple was connected to a Tag Celectray "2-second" recording potentiometer. The sample was

placed in an alundum boat containing cast iron chips as shown in Fig. 2, and the whole assembly heated in a muffle furnace supplied with an atmosphere of dried and purified commercial nitrogen. The gas was dried by passing through successive tubes of calcium chloride, ascarite, dehydrite, and phosphoric anhydride. Oxygen was removed by passing the dried nitrogen through a muffle furnace at 1100 degrees Fahr. packed with copper gauze. This combination of dry

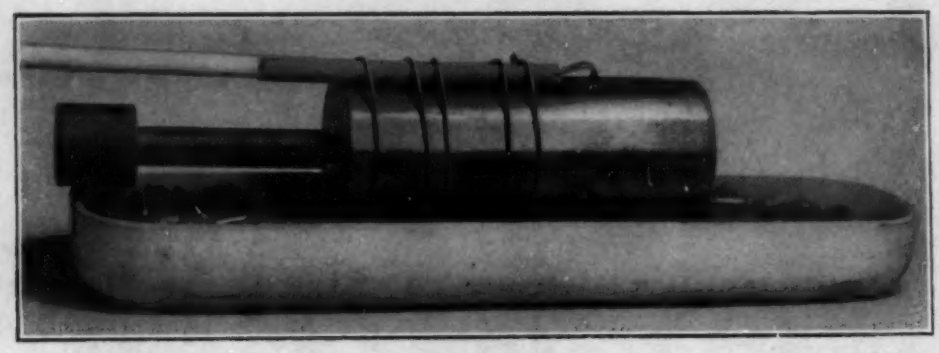


Fig. 2—Method of Affixing Thermocouples to Samples. Sample Shown in Alundum Boat Containing Cast Iron Chips.

nitrogen and cast iron chips produced no visible carburization or decarburization on any sample. The samples were held for ½ of an hour at the hardening temperatures shown in Table II, but it took about 1 hour for the samples to come to temperature, which meant a total time in the furnace of 1½ hours. The samples were then quenched in a tester similar to that of Jominy and Boegehold (5).

Metallographic Examination—When cooled to room temperature, the thermocouple was removed, and the flat, on which no thermocouple had been welded, was polished and etched for metallographic examination. Between 15 and 30 four by five-inch photomicrographs were taken of areas at definite positions along the bar. The photomicrographs were taken at ×100, ×500, and ×1000 depending on the fineness of the constituent under observation. The quantities of various microconstituents (martensite, fine pearlite, and ferrite) were quantitatively determined on each photomicrograph by counting squares as described by Lightner and Herty (6), or by a modification of the line segment method described by Polushkin (7). The two different methods are in good agreement.

Vickers pyramid hardness was determined along the same flat on which the metallographic examination had been made, using a ⅔-inch objective with a 10-kilogram load.

Cooling Data Determination—For determining the cooling characteristics of the bars, a thermocouple was again welded to the sample, but this time it was welded to the flat on which hardness had been determined and photomicrographs taken. The bar was then heated and cooled in the manner previously described. This reheating and quenching was repeated a number of times with a new

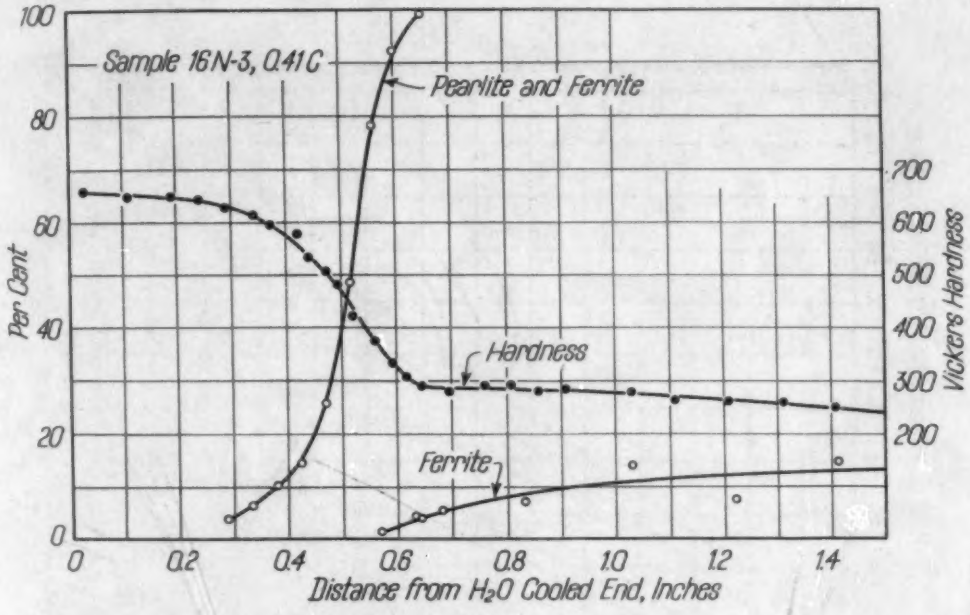


Fig. 3—Example of Master Curve.

thermocouple always welded at a different distance from the water-cooled end so that the cooling characteristics along every bar examined was thus known.

Plotting the Data—A series of master curves were constructed similar to the one in Fig. 3, showing the variations of hardness, fine pearlite plus ferrite, and ferrite as a function of the distance from the water-cooled end. At the rapidly cooled end, of course, the structure consisted of 100 per cent martensite. The amount of this constituent gradually decreased, or the amount of fine pearlite plus ferrite gradually increased, as the distance from the water-cooled end increased. For example, at 0.5 inches (Fig. 3) the structure consisted of 40 per cent fine pearlite plus ferrite and 60 per cent martensite. At 0.65 inches, there was 100 per cent fine pearlite plus ferrite, of which 5 per cent was ferrite. The amount of ferrite increased with further increase in distance from the water-cooled

end. The hardness decreased along the bar with increasing amounts of ferrite and fine pearlite.

Various cooling criteria have been published in the literature as a means of evaluating cooling data. Jominy and Boegehold have published cooling data for the time required to cool from 1100 to 900 degrees Fahr. (595 to 480 degrees Cent.), and Digges (8) has used the time to cool from 1110 to 930 degrees Fahr. (600 to 500

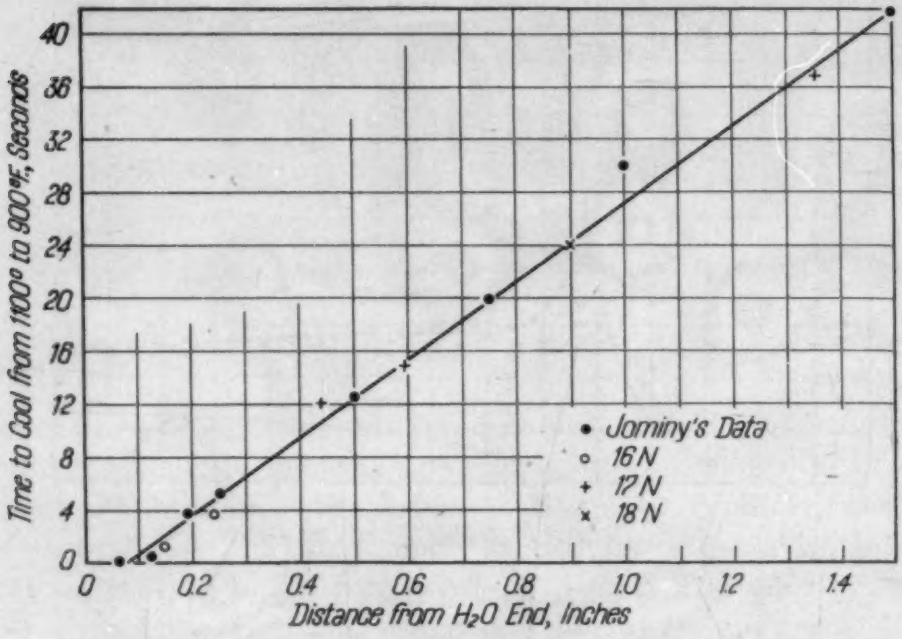


Fig. 4—Cooling Time Curve for D-type Bar.

degrees Cent.) as a critical cooling rate criterion. Grossmann, Asimow, and Urban (9) use the time to cool from the quenching temperature to a temperature halfway down to that of the quenching liquid. The "time to half temperature" criterion has the advantage that it involves the measurement of a larger quantity and, therefore, the accuracy is better, but the theoretical reason for such a correlation is not obvious. Other investigators have used cooling rate at a given temperature, or the average rate over a range of temperature.

It was felt that the time to cool over a range of temperature in the vicinity at the "nose" of the "S-curve" was the better method for correlating cooling data since the decomposition of austenite is most rapid in this temperature range. In this investigation, the criterion used in correlating the amount of fine pearlite plus ferrite

was the time to cool from 1100 to 900 degrees Fahr. (595 to 480 degrees Cent.), which is in the vicinity of the "knee" of the "S" curves for these steels. This time to cool from 1100 to 900 degrees Fahr. (595 to 480 degrees Cent.) was plotted against distance from the water-quenched end, an example of which is shown in Fig. 4. Previously published data by Jominy (5) has also been plotted in Fig. 4, and the agreement is very good. Similar curves were also drawn cor-

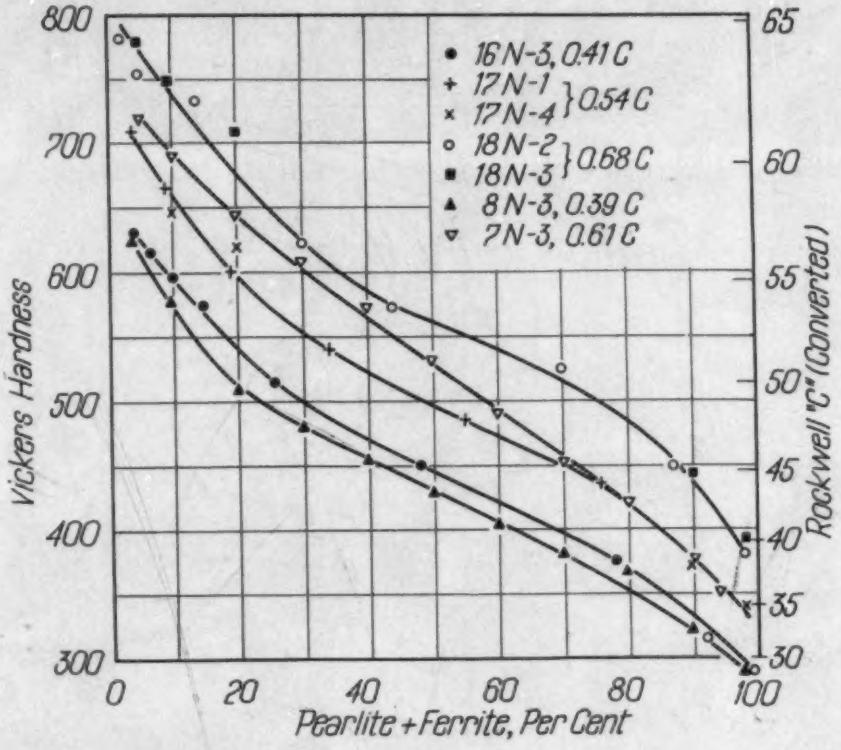


Fig. 5—Effect of Varying Microstructure on Hardness.

relating the time to cool from 1350 to 1050 degrees Fahr. (730 to 565 degrees Cent.) with distance along the bar. This latter time interval was used for correlation with the varying amounts of ferrite formed along the length of the test bar. This temperature range was used because it is the region at subcritical temperatures where ferrite precipitates during isothermal decomposition of austenite.

Results

From the curves described above, it was possible to correlate the data on the master curves with the cooling times. On the curves

which follow, experimental data are identified in the following manner: 16N-3-.41 C (Fig. 3) means steel No. 16 (see Table I), sample No. 3, containing 0.41 per cent carbon.

Effect of Variations in Microstructure on Hardness—Fig. 5 shows the effect of increasing quantities of pearlite and ferrite (or decreasing quantities of martensite) on the hardness values for

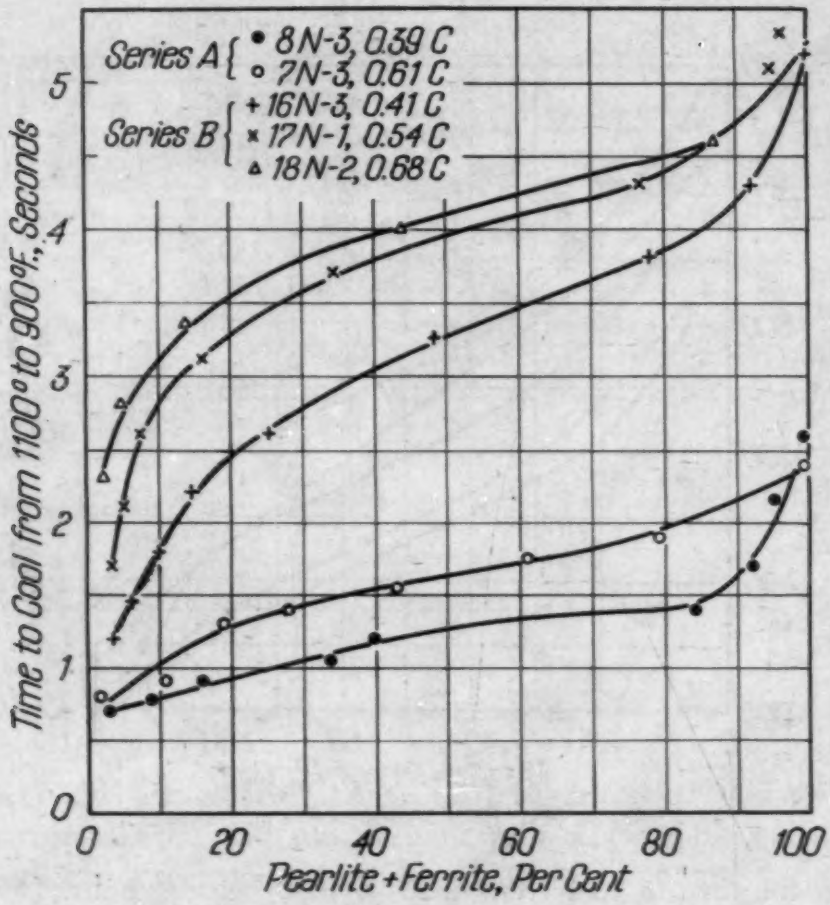


Fig. 6—Effect of Cooling Time From 1100 to 900 Degrees Fahr. (595 to 480 Degrees Cent.) on the Amount of Pearlite plus Ferrite Formed During Cooling.

various carbon contents. It is to be noted that the hardness decreases continuously with increasing amounts of fine pearlite plus ferrite, and that the hardness is higher for a given percentage of fine pearlite plus ferrite the higher the carbon content of the steel.

Effect of Cooling Time on the Formation of Pearlite Plus Ferrite—Fig. 6 shows the effect of the time to cool between 1100 and 900 degrees Fahr. on the amount of pearlite plus ferrite formed

Fig. 7—Sample 16N-3 (0.41 Per Cent Carbon), Showing Ferrite at Grain Boundaries Before Martensite has Completely Disappeared. × 100.
Fig. 8—Same Sample as Fig. 7. × 1000.

for different carbon contents. Steel No. 5 was omitted from the data since the steel formed so much ferrite during the quench that it was difficult to accurately determine the amount of fine pearlite at any given position on the bar. The abscissa is labeled pearlite plus ferrite in Fig. 5 since ferrite begins to appear at the grain boundaries before the martensite has completely disappeared, as

Fig. 9—Sample of Steel 18 (0.68 Per Cent Carbon), Showing Practically No Ferrite in the Grain Boundaries in the Presence of Martensite. × 1000.

shown in Figs. 7 and 8. The effect decreases in magnitude with increasing carbon content, as shown in Fig. 9.

From Fig. 6, it should be noted that increasing carbon content seems to affect the inception of transformation to fine pearlite plus ferrite more than it does the end of the decomposition. In comparing Series A and B, the grain size in Series B is more effective in retarding the end of the transformation than it does the beginning.

Critical Cooling Time Data—For determining the "critical cooling time," 5 per cent fine pearlite and the time to cool from 1100 to 900 degrees Fahr. (595 to 480 degrees Cent.) were used as criteria. Five per cent of fine pearlite was chosen because interpolation on the master curves at 5 per cent offered greater accuracy than smaller amounts, since experimental data for quantities of fine pearlite both larger and smaller than this quantity were available. The data for the two series were plotted in Fig. 10 along with some similar data published by Digges (8). It will be observed the time increases with increasing carbon content and also with increasing grain size, the effect of grain size being greater in the higher carbon steels.

Fig. 11 shows the effect of carbon content on the "critical cooling time" for ferrite precipitation for Series A, using the criteria of 4 per cent ferrite and the time to cool from 1350 to 1050 degrees Fahr. (730 to 565 degrees Cent.). Four per cent ferrite was used because the accuracy of interpolation at 4 per cent on the master curves was good since values greater and less than this amount were available in all samples of Series A. A similar curve was not determinable for Series B since there was so little ferrite present in steels Nos. 17 and 18. The smaller amounts of ferrite obtained in Series B are brought out in Fig. 12 which shows the amount of ferrite produced in all samples with a constant cooling time from 1350 to 1050 degrees Fahr. (730 to 565 degrees Cent.) equal to ten seconds.

Discussion of Results

Table III has been compiled for comparing the data of Fig. 5 at 50 per cent fine pearlite plus ferrite with that previously published by Bain (10). (Private communication from Grossmann.) Both

Table III
Rockwell "C" Hardness at 50 Per Cent Martensite

Percentage of Carbon	Grossmann's Data	Present Investigation Data Converted from Vickers Hardness	
		Scott's (11) Conversion	A.S.M. Handbook (12)
0.41	39-41	45	44
0.54	45-47	49	47
0.68	50-52	53	52

the Scott conversion and the A.S.M. Handbook conversion are given here since there is considerable discrepancy in these two conversion tables from Rockwell C-50 to 70. The agreement with Grossmann's data is fairly good when it is considered that the amount of martensite was visually estimated by Grossmann, that the data of the present investigation were interpolated from curves whose slopes are rapidly changing, and that a conversion from Vickers to Rockwell hardness was necessary for the comparison made in Table III.

Fig. 6 indicates that carbon content in the range investigated does not appreciably affect the time required to produce 100 per cent fine pearlite plus ferrite. To check this point, "D" type samples (Fig. 1) were made from each steel of Series B and were heated and quenched in the manner previously described. The hardness data

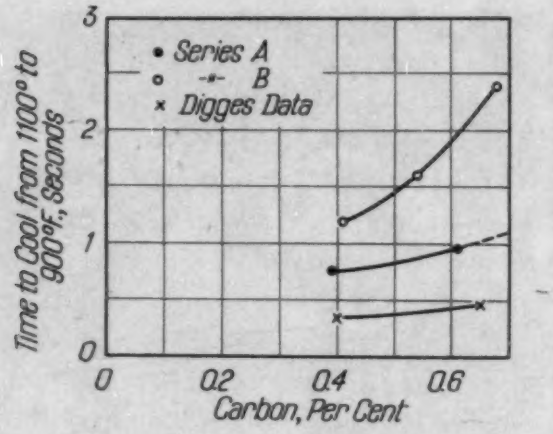


Fig. 10—Effect of Carbon Content on Critical Cooling Time.

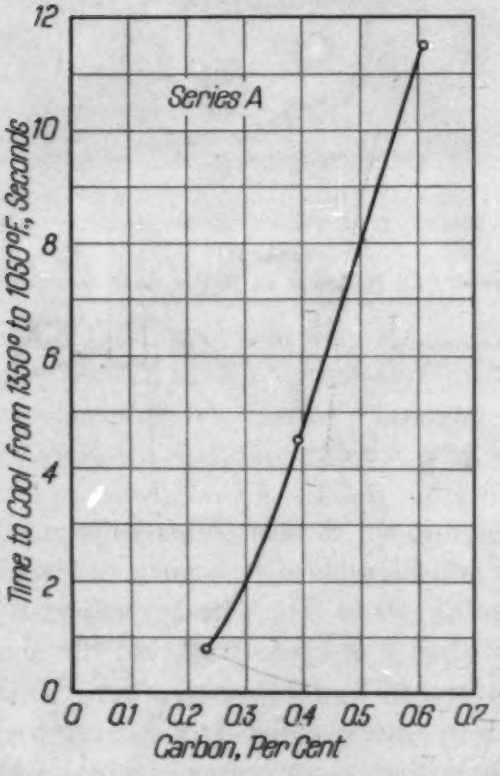


Fig. 11—Effect of Carbon Content on Critical Cooling Time for the Formation of 4 Per Cent Ferrite.

for these samples are plotted in Fig. 13. It can be seen that the curves all flatten off between 0.25 and 0.28 inches from the water-cooled end, which confirms the fact that the carbon content does not

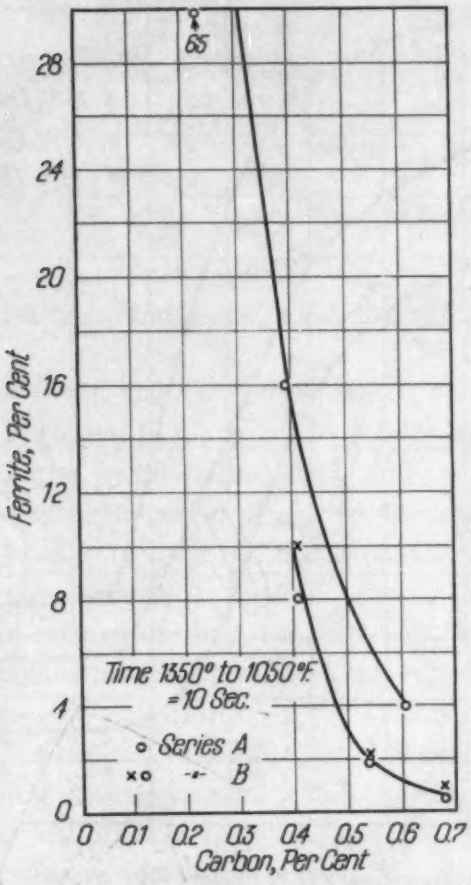


Fig. 12—Effect of Carbon Content on Amount of Ferrite Formed with a Constant Cooling Time Between 1350 and 1050 Degrees Fahr. (730 and 565 Degrees Cent.) Equal to 10 Seconds.

appreciably affect the time required to produce 100 per cent fine pearlite plus ferrite.

Fig. 6 shows the time required to form 100 per cent fine pearlite plus ferrite is about 5¼ seconds in Series B and 2½ seconds in Series A. This may be attributed to the difference in grain size between Series A and B. To confirm this observation, a sample of steel No. 16 was coarsened to an austenitic grain size of 1-2 by heating to 1700 degrees Fahr. (925 degrees Cent.), furnace-cooled to the quenching temperature, and quenched in the end quench tester (5). This sample is compared with 16N-3, austenitic grain size 2-7 in Fig. 14. Coarsening the grain size of this steel increases the time required to form 100 per cent fine pearlite plus ferrite, which confirms the observation made from Fig. 6.

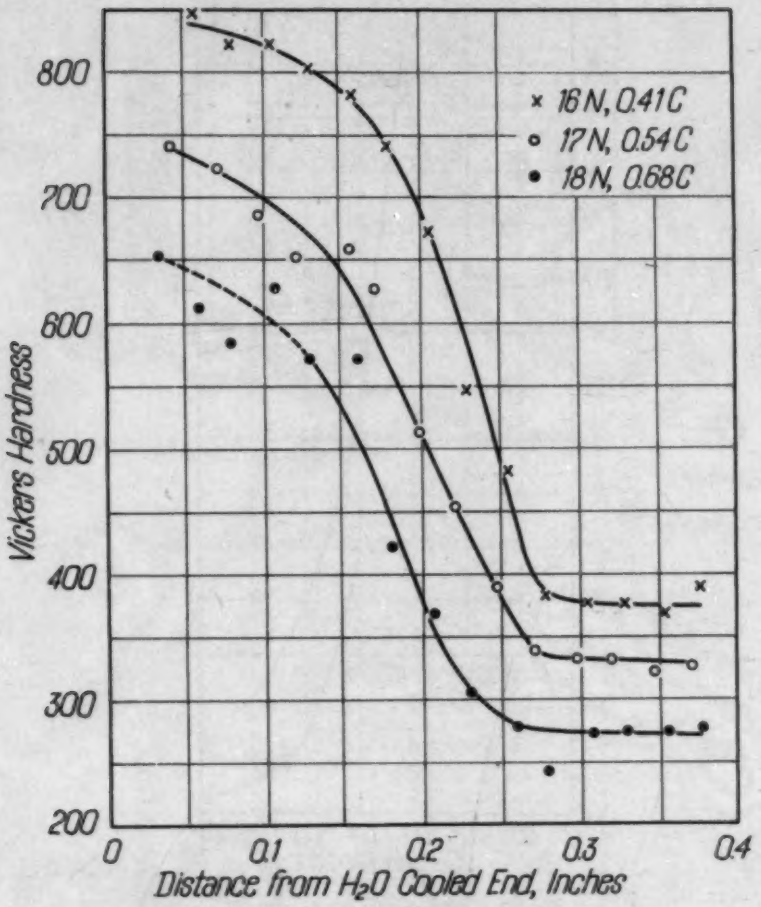


Fig. 13—Effect of Carbon Content on the Hardness Curves Obtained on Standard Jominy Test Bars.

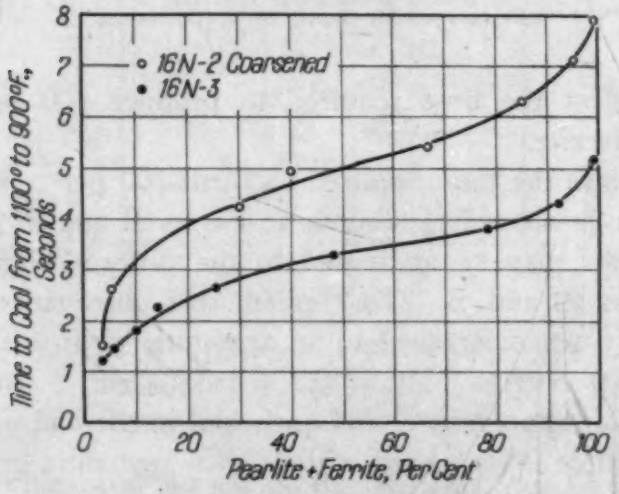


Fig. 14—Effect of Coarsening the Austenitic Grain Size of Steel No. 16 (0.41 Per Cent Carbon) on the Time Required in Cooling From 1100 to 900 Degrees Fahr. (595 to 480 Degrees Cent.) for a Given Amount of Pearlite Plus Ferrite.

Table IV
Comparison of Digges' Investigation With This Investigation

	Digges	This Investigation
Microstructure criterion	1-3 Per Cent Fine Pearlite*	5 Per Cent Fine Pearlite**
Cooling time criterion	1110-930 degrees Fahr.	1100-900 degrees Fahr.
Percentage of manganese	0.46	0.80
Grain size	5	Series A—8 Series B—2-7

*Visually estimated.
**Interpolated on master curve.

This effect of grain size can be explained on the basis of nucleation and rate of growth (13). In these steels, the nucleation of fine pearlite begins at the grain boundaries, and, assuming the rate of growth is approximately constant for both small and large grain sizes, it merely takes longer for the completion of radial growth in the coarse-grained samples.

The data on critical cooling time in Fig. 10 to produce 5 per cent pearlite is somewhat higher than that reported by Digges (8). Although the order of magnitude of the critical cooling time of this work compares favorably with that of Digges, certain differences existed in the two investigations which have been summarized in Table IV. These differences may account for the variations shown in Fig. 10. The divergence of the curves for Series A and Series B at increasing carbon content indicates clearly that, with increase in hardenability due to composition, the effect of grain size increases as previously reported by Grossmann and Stephenson (14).

Herty, Lightner, and McBride (3) have shown that the rate of ferrite formation during isothermal decomposition between the A_1 and A_3 critical temperatures is higher for fine-grained than for coarse-grained steels. This same effect of grain size on ferrite precipitation during continued cooling to room temperature is shown in Fig. 12.

Summary

Quantitative data for the continuous cooling of hypoeutectoid steels are presented correlating:

1. The percentage of martensite and hardness in partially transformed areas as a function of carbon content.
2. The time to cool from 1100 to 900 degrees Fahr. (595 to

480 degrees Cent.) and percentage of pearlite plus ferrite in partially transformed areas as a function of carbon content and grain size.

3. Critical cooling time curves, using the criteria of 5 per cent fine pearlite plus ferrite and the time to cool from 1100 to 900 degrees Fahr. (595 to 480 degrees Cent.) as a function of carbon content and grain size.

4. Critical cooling time curves using the criteria of 4 per cent proeutectoid ferrite and time to cool from 1350 to 1050 degrees Fahr. (730 to 565 degrees Cent.) as a function of carbon content and grain size.

ACKNOWLEDGMENT

The authors are much indebted to Messrs. R. S. Archer of the Republic Steel Corporation and S. F. Urban of the Carnegie-Illinois Steel Corporation for supplying the steels used in this investigation.

Bibliography

1. E. S. Davenport, "Isothermal Transformation in Steels," TRANSACTIONS, American Society for Metals, Vol. 27, December, 1939, p. 837.
2. R. A. Grange and J. M. Kiefer, "Transformation of Austenite on Continuous Cooling and Its Relation to Transformation at Constant Temperature," TRANSACTIONS, American Society for Metals, Vol. 29, March, 1941, p. 85.
3. C. H. Herty, Jr., M. W. Lightner, and D. L. McBride, "The Effect of Deoxidation on the Rate of Ferrite Formation in Plain Carbon Steels," *Carnegie Institute of Technology Cooperative Bulletin 64,* 1934.
4. J. A. Verö, "The Effect of Cooling Rate on the Quantity of Proeutectoid Ferrite," *Royal Hungarian Palatine*—Joseph University of Technical and Economic Sciences—Publication Department of Mining and Metallurgy, Vol. 9, 1937, p. 192.
5. W. E. Jominy and A. L. Boegehold, "A Hardenability Test for Carburizing Steel," TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 574.
6. M. W. Lightner and C. H. Herty, "The Transverse Impact Strength of Plain Carbon, Normalized Steels," *Carnegie Institute of Technology Co-operative Bulletin 59,* 1932.
7. E. P. Polushkin, "Determination of Structural Composition of Alloys by a Metallographic Planimeter," *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 71, 1925, p. 669.
8. T. G. Digges, "Effect of Carbon Content on the Critical Cooling Rate of High Purity Iron Carbon Alloys and Plain Carbon Steels," *Journal of Research,* U. S. Bureau of Standards, Vol. 20, 1938, p. 571.
9. M. A. Grossmann, M. Asimow, and S. F. Urban, "Hardenability, Its Relation to Quenching, and Some Quantitative Data," *Hardenability of Alloy Steels,* American Society for Metals, 1939, p. 124.
10. E. C. Bain, "Functions of the Alloying Elements in Steel," American Society for Metals, 1939, p. 162.

11. H. Scott and T. H. Gray, "Relation Between the Rockwell 'C' and Diamond Pyramid Hardness Scales," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 369.
12. METALS HANDBOOK, American Society for Metals, 1939, p. 127.
13. R. F. Mehl, "The Physics of Hardenability," *Hardenability of Alloy Steels,* American Society for Metals, 1939, p. 14.
14. M. A. Grossmann and R. L. Stephenson, "The Effect of Grain Size on Hardenability," TRANSACTIONS, American Society for Metals, Vol. 29, 1941, p. 4.

DISCUSSION

Written Discussion: By Morse Hill, Jr., metallurgist, Materials Laboratory, Materiel Division, U. S. Army Air Corps, Wright Field, Dayton, Ohio.

The authors have considerably added to the quantitative knowledge of hardenability and have described a simple method of studying the final results of austenite decomposition at various rates. The preparation of specimens for microscopic study in this connection may be greatly facilitated by the use of electropolishing, especially if the examination is visual and at the higher powers of magnification. Acceptable results can be obtained almost on the first trial and with practice it is possible to find satisfactory areas for photography.

In the course of an investigation now being conducted by the Materiel Division numerous specimens of the authors' "type D", taken from most of the aircraft steels, have been examined. It appears that the usual series of final structures obtained in such specimens of carbon and alloy steels is not a simple progression from martensite to pearlite as the cooling rate decreases. The authors imply that the important change is in the amount of ferrite plus pearlite present. There are also many other regular variations in amount and nature of constituents. These take place over ranges of cooling rates which vary in extent with the composition and prior history of the specimen.

The variation in structure in a S.A.E. 1045 specimen will appear at × 1500 somewhat as follows: At the hard end there will be a white martensite with possibly some retained austenite at the very end. The appearance is that of a network of acicular crystals. Progressing toward the slower cooling end the needles tend more and more to appear as parallel groups, and the structure becomes more gross. Concurrently their edges blacken almost like a deposit of soot. At length the structure is almost completely black and some ferrite has separated. At slightly slower rates of cooling, the blackness is supplanted by clumps of discreet particles often arranged in groups of parallel lines but generally not exhibiting an organized structure. These particles become larger up to a certain size until the entire structure consists of clumps of particles and ferrite. At about this point there appear, for a very small range of cooling rates, larger brilliant particles, reminiscent of spheroidized carbides which constitute a small portion of the structure. As the cooling rates lessen, the particles which supplanted the black constituent begin to be larger and then to appear in more or less ordered arrangements and the first traces of definitely lamellar pearlite appear. These traces are parts of dark grains which have

no definite internal arrangement otherwise. Coincidentally with this, the ferrite begins to exhibit grain boundaries and in many of them are small groupings of black dots. From this point on the change is a rather orderly progression. The pearlite lamellae become longer and straighter and the range of spacings increases. The ferrite boundaries become more definite and continuous around the grains. The clumps of black dots tend more and more to exhibit structure tending toward the lamellar. At the slowly cooled end the structure is almost a simple pearlite plus ferrite.

Observation of the structural variations naturally raises questions. In a particular area of a particular grain, is the final structure determined by the structure of the initial austenite decomposition products or as austenite decomposition proceeds at lowering temperatures does each increment of product have a structure characteristic of its temperature of formation? Are or are not the structures found in these bars predictable by use of the "S-curve"? Can the whole process of change be visualized by considering pearlite a structure into which the carbides are seeking to arrange themselves but from which they are prevented by lack of mobility induced by temperature or alloying elements? More studies like the authors may bring the answers nearer. However, it would seem that a study of the cooling curves as compared with those of specimens of equal thermal diffusivity might show informative inflections and changes in slope.

Written Discussion: By W. E. Jominy, metallurgist, Engineering Department, Chrysler Corp., Detroit.

This paper contains data which is well worth having. I am particularly pleased to find the good correlation between results in this paper and those which were presented in a paper by A. L. Boegehold and myself at the A.S.M. Convention in 1937. This correlation is shown in Fig. 4, and so far as I know represents the first independent check of the measurements made on cooling time of the end-cooled bar.

Perhaps attention should be called to the bars shown in Fig. 1. The bars marked A and D are the more or less standardized bars used in the end-cooled method for measuring hardenability. However, bars B and C have been modified by the authors to carry on a certain part of their research and these differ from the commonly used bars. While I feel that it is perfectly satisfactory to use bars which are not standard for a specific purpose as the authors did here, I hope bars B and C will not be mistaken for standard bars by those who wish to make ordinary hardenability tests.

The curve of Fig. 11, showing the critical cooling time for the formation of 4 per cent ferrite, is particularly interesting data to those of us who are interested in fatigue. I believe it is commonly held that the precipitation of ferrite in quenching seriously affects fatigue values and the knowledge of cooling rate necessary to prevent appreciable ferrite precipitation is worth having. It would be helpful if the authors could give us the hardness values that accompany 4 per cent ferrite for the various steels tested.

Written Discussion: By J. L. Burns, superintendent, Wire Division, Republic Steel Corp., South Chicago, Illinois.

This paper by Messrs. Thomson and Siebert is another contribution of defi-

nite data intended to bring about eventual predictions of results. There is much to be saved in time and procedure when this is achieved.

For example, if it were possible to evaluate each chemical (or other) addition or any combination thereof with respect to critical cooling rate, imagine the saving in time to be expected! Most studies of this kind are intended toward anticipation of hardenability results.

This hardenability problem resolves itself into two main problems, namely: (1) How hard will a steel become at the surface? (2) To what depth will the piece harden?

It has been shown that the surface hardness after cooling is dependent solely upon the carbon content, provided that:

A. The carbon is in solution prior to cooling.

B. The cooling is sufficiently fast to attain or exceed the critical cooling rate.

C. No appreciable austenite is retained.

Good heat treatment usually demands that "A" and "B" be achieved. Item "C" is a statement of conditions prevailing in the heat treatment of practically all of our heat treated carbon and medium alloy steels after water quenching.

The second problem on depth of hardening is far more complex and depends upon all of the chemical elements present, the austenite grain size, and perhaps some other factors not yet thoroughly understood. Naturally the complexity of this problem is great.

A paper such as the one under discussion is a welcome addition to our quantitative knowledge and it is hoped that the authors will bring more quantitative data forward for the evaluation of elements other than carbon with respect to the critical cooling rate.

Oral Discussion

C. B. Post:[1] Mr. Chairman, the authors are using a time of cooling between certain temperature zones as their parameter in these hardenability studies. Are there any investigations which show the correlation between parameters involving time to cool between certain temperature zones and the rate of cooling past certain given temperatures? I would like to ask these authors whether they have any such correlations, or if correlations such as these have been published? It would serve a good purpose if we had some information on this point.

Authors' Reply

We wish to thank the people who have discussed our paper.

Mr. Hill's interesting discussion is primarily concerned with the variations in microstructure at various distances from the water-cooled end of the bar. The question of terminology is a debatable subject at the present time and the authors chose to call all of the dark etching constituent, which transformed at a high temperature, pearlite. This dark etching constituent did not always appear lamellar at × 1000. As to whether or not the final structure on a con-

[1]Metallurgical department, The Carpenter Steel Co., Reading, Pa.

tinuous cooled specimen is determined by the initial austenite decomposition products was not ascertained in this investigation.

In reply to Mr. Jominy's request for information concerning the hardness when the microstructure contains 4 per cent ferrite, the authors submit the following:

Hardness for Microstructure Containing 4 Per Cent Ferrite

Steel No.	Per Cent Carbon	Vickers Hardness
5	0.23	380
8	0.39	290
16	0.41	290
7	0.61	325

It can be seen that the hardness at 4 per cent ferrite does not always increase with increasing carbon content. This is due to the fact that steel No. 5 contains about 85 per cent low carbon martensite in addition to the pearlite and ferrite, while the higher carbon contents contain little or no martensite when the ferrite reaches 4 per cent. In the low carbon steels, the presence of appreciable amounts of martensite controls the hardness, whereas in steels No. 8, 16 and 7, the hardness is dependent upon the carbon content and the fineness of the pearlite formed.

We heartily endorse Mr. Jominy's hope that no one will adopt the Type "B" and "C" bars as standard hardenability bars, and it was not our intent that they should be used as such. We only deviated from the standard bar dimensions to obtain the different rates of cooling which were necessary for this particular investigation.

Mr. Post directs attention to the authors' use of time to cool over a given temperature interval rather than the cooling rate at a given temperature. In the oral presentation of the paper, time did not permit a discussion of the reasons for the choice of this parameter, which are presented in the written text of the paper. To the best of the authors' knowledge, no correlation between the time to cool over a given temperature interval and the rate of cooling at a given temperature has been published. The authors are working on a correlation between these two parameters at the present time.

The authors acknowledge Mr. Burns' discussion, and hope further studies of this type will be carried out which will lead to a better understanding of the hardenability problem as outlined by him.

LOW EXPANSION ALLOYS FOR GLASS-TO-METAL SEALS

By W. E. Kingston

Abstract

This development of the "lock-in" radio tube necessitated new low expansion alloys for glass-to-metal seals. The qualities desired are discussed with data on 65 alloys investigated and the technique of their use. Additions of the following elements tend to raise the expansion of known low expansion alloys: aluminum, copper, iron, nickel, chromium, silicon, manganese, beryllium and columbium. An exception to these is the iron-chromium system. A series of iron-nickel-chromium alloys developed proved satisfactory. With the addition of 0.5 per cent of carbon to the basic alloy the material retained its hardness even after thorough annealing. By varying the principal constituents of these alloys, coefficients of expansions ranging from 70 x 10^{-7} to 120 x 10^{-7} per degree Cent. can be obtained. Due to the great inherent strength of the bond between these metals and their associated glasses, they should be well adapted for seals to glass where large mechanical stresses are encountered. These alloys are low in cost and can be made successfully by standard metallurgical methods. This series of alloys have excellent stainless properties.

THIS paper is not intended as a hypothetical discussion of glass-to-metal seals, but rather as a report of the author's experiences in the study of alloys for this purpose, and to bring out some practical information on the subject, resulting from the study of known alloys and the development of new alloys for this use.

In the early days of the incandescent lamp industry, platinum wire was used with lead glass to form a glass-to-metal seal. Due to the extremely high cost of the metal, efforts were made to cut down the amount used by introducing a three-piece lead, in which a short length of platinum, 4 to 6 millimeters long, was welded at each end to a copper or nickel lead wire. The platinum to lead glass seal was not a particularly good match, as shown in Fig. 1, but, with proper

The author, W. E. Kingston, is chief metallurgist, Hygrade Sylvania Corp., Emporium, Pa. Manuscript received September 5, 1940.

annealing of the seal gave satisfactory results. In any case the use of this material is only of historical value, due to its high cost.

Since about 1913, when Eldred invented the "dumet" lead wire, this material has been used quite generally for sealing with lead glass (1)[1] in both the incandescent lamp and radio tube industry.

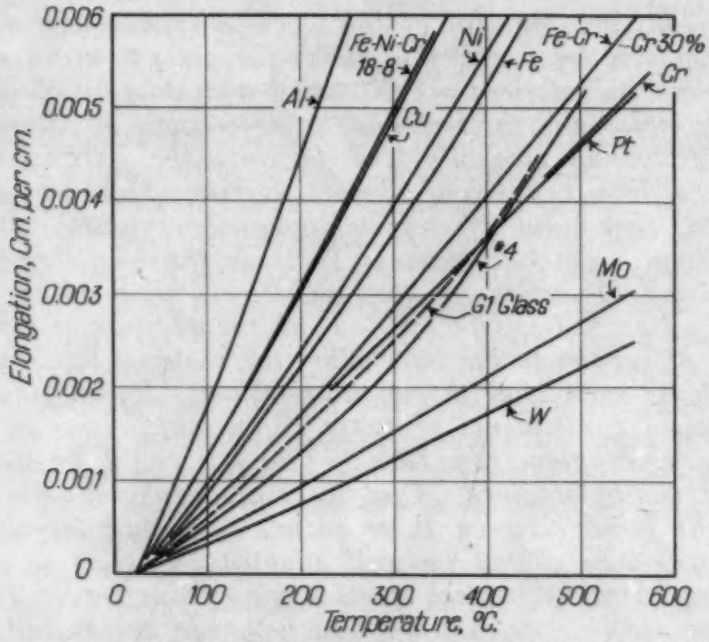


Fig. 1—Thermal Expansion Curves.

These seals have been satisfactory when used with comparatively small diameters of wire (under 0.040 inch). However, in so far as expansion characteristics are concerned, the "dumet" does not match very closely the glass with which it is used and radial compression strains remain in the seal.

"Dumet" as it is usually used, is a bimetal having an alloy core of 42 per cent nickel, balance iron, around which a copper sleeve is drawn. This composite slug is first swaged and then drawn down to the desired wire size. The volume of copper is held at approximately 25 per cent of the total. Since "dumet" is comparatively expensive, it is usually used in a three-piece weld, in which a short section of dumet, from 4 to 6 millimeters long is electrically welded to copper or nickel leads. The dumet section is sealed into the glass while the two leads extend outwards from each side of the seal.

Since the expansion of the core is substantially less than the

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

glass with which it is used, a seal having radial compression results. The outer copper sheath tends to flow somewhat and thus relieves a large percentage of the strains caused by the mismatch of the alloy core and the glass. With dumet leads above 0.025 inch in diameter the seals are badly strained and since the adherence of the oxide to the copper sheath is weak seals are not considered safe.

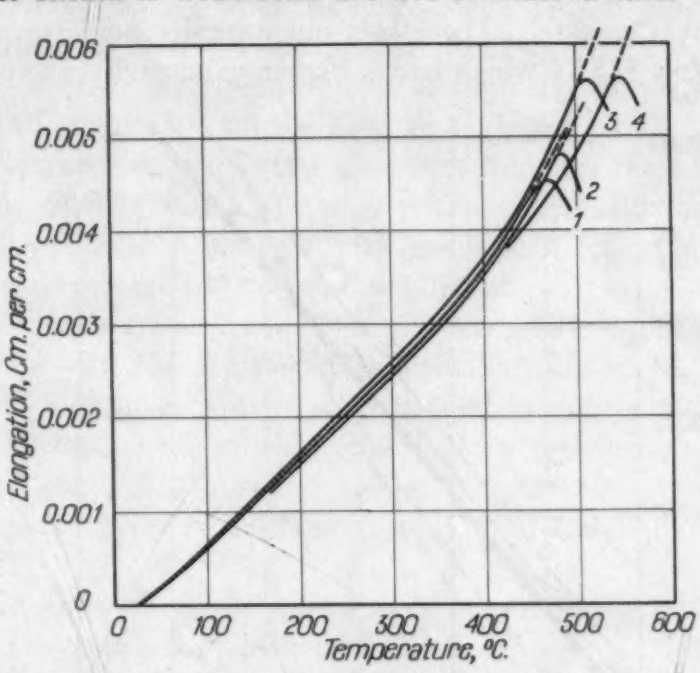


Fig. 2—Thermal Expansion Curves of Lead and Lime Glasses.

During the past few years the Hygrade Sylvania Corporation has pioneered in the development of the "lock-in" radio tube. In this tube it is necessary to use metal pins, which are used to form contact with the socket; and which form an integral part of the tube itself, and as such, must be capable of forming a vacuum-tight seal with the lead glass used in the tube stem. (See Fig. 8) Also these pins must be made from a material having low electrical resistance and one having sufficient mechanical strength to withstand bending due to normal tube handling. Since obviously "dumet" was undesirable due to the large size pin needed to insure mechanical rigidity (0.050 inch diameter or greater), and due to the high comparative cost of "dumet", and for other reasons, other available alloys were investigated.

A large number of radio tubes were made up using as pin material an alloy containing 27 to 30 per cent chromium, balance iron.

This alloy which is known commercially as "446 alloy" or "55 alloy" will be referred to in this paper as alloy No. 7. Referring to Fig. 3 it will be seen that the expansion of alloy No. 7 is considerably higher than Corning type G_1 lead glass which will be hereafter referred to as glass No. 1, and seals between alloy No. 7 and glass No. 1 resulted in intense radial tension strains around the pin and were obviously unsafe. Therefore, our supplier made up a special glass, Corning 125AJ which had a higher expansivity (some 12 per

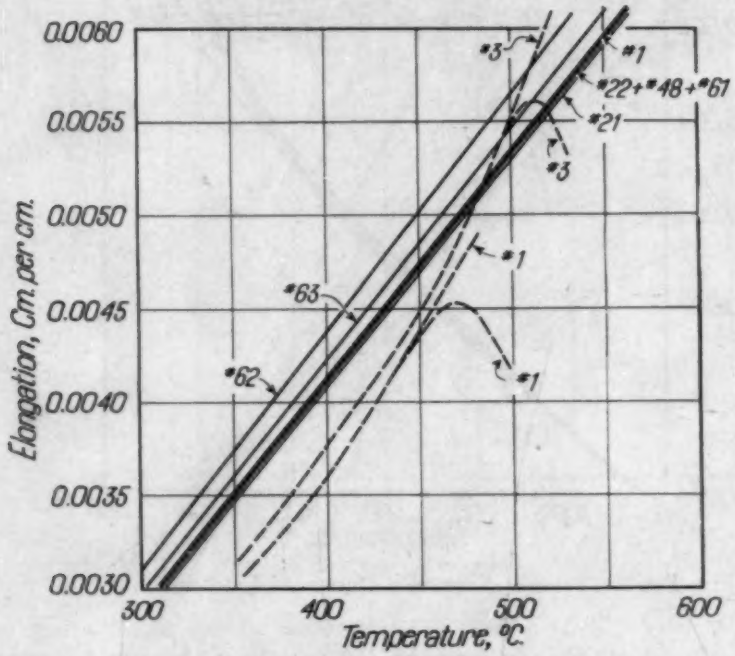


Fig. 3—Thermal Expansion Curves.

cent) than No. 1 glass. This glass will be designated as glass No. 3 and its expansivity is shown as a function of temperature in Figs. 2 and 3. Fig. 2 shows elongation versus temperature curves for the four types of glasses discussed in this paper. Their approximate composition is given in Table II. Although the expansivities of alloy No. 7 and glass No. 3 do not match at all temperatures, they are fairly close in the annealing range and also at room temperature. With suitable annealing this alloy and the special No. 3 glass made fairly strain-free seals which were satisfactory in so far as glass-to-metal seals were concerned.

However, when the No. 3 glass cup was sealed to the No. 4 lime glass bulb (Corning G-8) considerable strain was set up due to the differences in expansivity of the glass. This was also true in the

case of sealing the (Corning G-12) No. 2 glass exhaust tube into the bottom of the cup. This is shown in Fig. 8. These mismatches in glasses resulted in an appreciable loss of radio tubes, since cracks developed due to these strained conditions.

Another disadvantage of the special No. 3 glass was its inferior electrical characteristics when compared with Nos. 1 and 2 glasses. This difference is clearly shown in Fig. 7. Since some of the radio tubes may operate at a temperature as high as 200 degrees Cent. (390 degrees Fahr.), it can be seen that glasses Nos. 1 and 2 are distinctly superior to the special glass No. 3 in this respect. Therefore it was obvious that a pin alloy which would seal satisfactorily to glass Nos. 1 or 2 would be advantageous both from a quality and lower glass shrinkage (breakage) standpoint.

Since there were no commercial alloys available which would seal satisfactorily with No. 1 glass for our particular purpose, it was decided to make an investigation of low expansion alloys and, if necessary, to develop alloys which would form a satisfactory seal with Nos. 1 or 2 glass.

This paper gives some data on alloys and technique of use investigated.

In any study of glass-to-metal seals several factors must be considered. They are as follows:

1. The expansivity of the glass and metal must match closely over a given temperature range.

2. It should be possible to obtain a layer of oxide on the surface of the metal which will adhere tightly throughout all processing involved in the forming of the glass-to-metal seal.

3. This oxide coating must be of such a nature and must be thick enough, so that it prevents the formation of iron oxide, or other loosely adhering oxides on the surface of the metal during subsequent processing.

4. This oxide coating should dissolve (wet) mutually with the glass.

5. It is desirable that the oxide formed on the metal be of a sufficiently low electrical resistance so that it may be welded easily to other metals such as nickel and iron by electric spot welding.

6. It is essential that the alloy for the glass-to-metal seals be a reversible one, in so far as elongation is concerned and that no thermal critical points (allotropic transformations) occur in any temperature region that the finished article might be subjected to.

7. The alloys should be comparatively low in cost and should have compositions which are relatively easy to melt and must be capable of close reproduction in commercial quantities. (10,000-50,000-pound melts)

8. These alloys must be of such nature that their physical characteristics will allow normal hot and cold working of the material, without forming cracks, seams or other mechanical defects. Also it is desirable to have an alloy which is capable of being processed so that different degrees of hardness or ductility may be obtained.

These eight factors will be discussed in some detail.

1. *Thermal Expansion of Alloys and Glass.* It has previously been the contention of some authors on this subject that it is of extreme importance that the elongation of the metal and the glass must match closely over the entire range of temperatures, between the lowest operating temperature (approximately —40 degrees Cent.) and the highest annealing temperature of the glass, in order to obtain strain-free glass-to-metal seals. While this contention may be true in the case of glass-to-metal seals which are so constructed that the glass and metal cool at the same rate, or if production facilities are such that the seals can be annealed thoroughly, in most high production processes this annealing condition is costly and slow and therefore is rarely attained. In our particular case the glass-to-metal seals were made in glass cups in which 5 to 8 alloy pins were sealed (see Fig. 8). By far the largest portion of these pins are outside the seal and therefore the metal tended to cool at a much faster rate than the larger mass of glass. Even in the brief time consumed in transferring the article from the pin sealing machine to annealing oven the metal pins had cooled to a considerably lower temperature than the more massive glass body. Of course, it would have been possible to have used a large annealing oven which would have raised the entire temperature of the metal and glass above the annealing point of the latter and then cooled both at exactly the same rate until room temperature had been reached; however, this was not feasible from a manufacturing standpoint.

The above indicates the practical impossibility of taking advantage of a perfect elongation match of a metal and glass which are to be sealed together, unless very elaborate annealing methods are used. This is especially true when the metal cross section is comparatively large and when the metal part of the seal extends outside of the glass to any appreciable distance.

Therefore, the importance of the relative expansivities of the metal and glass becomes considerably less, except in two regions.

(a) It is of extreme importance that the expansions of the metal and glass match closely between the temperature limits bounded by the upper and lower temperatures to which the radio tube is subjected in actual use. (−40 to +200 degrees Cent.)

(b) The metal and glass expansions should match quite closely over the annealing range of the glass. In our particular study of glass-to-metal seals using No. 1 glass this corresponds to a temperature range between 400 and 450 degrees Cent. (750 and 840 degrees Fahr.).

We feel that between these two ranges of temperatures the expansions of the metal and glass may vary considerably, provided that the union between the oxide layer on the metal, and the metal itself is sufficiently strong, and that the transitory strains set up do not exceed the strength of the glass or the bond between the glass and oxide layer.

2. *Adherence of Oxide and Metal.* In the mass production of glass-to-metal seals, in order to obtain vacuum-tight seals having a large factor of safety in subsequent heating and cooling operations, during which large degrees of strain were set up between the glass and metal parts of the seal, it was found that it was essential that the bond between the oxide layer and the metal be very strong. In the particular series of alloys developed for this use, small quantities of special elements were added to obtain this condition. These additions were small enough in percentage of total constituents so that their effect on the expansion of the alloys was negligible.

3. *"Wetting" of the Oxide and the Glass.* Glass will combine or dissolve to some degree with most oxides of metals. With the special alloys developed by us, a strong bond was formed between the oxide layer and the glass.

4. *Protective Feature of Oxide Coating.* During the development of the new series of alloys for sealing with glass it became evident that the oxide coating had another very important function. It was found that a preliminary coating of chromium oxide (Cr_2O_3) was necessary in this particular series of alloys in order to prevent the formation of iron oxides and other complex oxides during subsequent processing. These undesirable scaly, loose, surface oxide layers resulted from the intense heating to which the alloy was subjected during the sealing process. In order to melt the glass quickly,

in high production equipment, it is often necessary to use highly oxidizing flames on the glass and metal parts. This is especially true when natural gas, with its low rate of flame propagation, is used as a fuel. During this operation the metal is often heated to a temperature in excess of 1100 degrees Cent. (2010 degrees Fahr.) and unless the metal has previously been covered by a very stable layer of oxide of sufficient thickness to protect the base metal from further oxidation, a scaly iron oxide will form on the surface of the metal preventing proper sealing.

The formation of this scaly iron oxide always results in poor glass-to-metal seals which tend to leak.

With the new series of alloys developed it was found that a definite thickness of chromium oxide must be placed on the alloy, prior to the sealing operation. By firing the alloy at a high temperature in an atmosphere of hydrogen which contained a specific percentage of water vapor, for a definite period of time, an oxide was obtained which satisfied all conditions. The thickness and nature of this oxide could be closely controlled in mass production.

Using pins of this new series of alloys, oxidized in the proper manner, large seals could be made which could be cooled in air, without annealing, and still be vacuum-tight, although naturally the glass body itself was badly strained. Successful glass-to-metal seals were made using metal rods having a diameter of 0.250 inch. This indicates the great factor of safety incorporated in this type of alloy and its associated oxide coating.

5. *Electrical Resistance of Oxide Layer.* Since it was difficult and costly to remove the oxide from the pins (metal lead wires) after the sealing operation, by chemical cleaning, in order to obtain a clean metal surface for welding it was necessary to develop an oxide whose electrical resistance was relatively low. This was accomplished in such a way that it did not affect the other functions of the oxide. Under proper processing conditions this resistance is uniformly low, and allows normal spot welding operations in production.

6. *Thermal Critical Points of the Metal.* Obviously any alloy for use in glass-to-metal seals should undergo no allotropic changes in crystal structure at any temperature between the softening point of the glass and the lowest possible operating temperature of the finished article. Although they are not shown on any of the attached curves dilatometric studies were made on the new series of alloys

between temperature ranges of from —75 to +1000 degrees Cent. (—85 to +1830 degrees Fahr.). These austenitic alloys did not undergo any phase changes over this temperature range.

The importance of this factor can be easily seen when one considers what would happen to a glass-to-metal seal if the metal part of the solidified seal underwent a change in crystal structure (with the associated change in volume) at some temperature at which the finished article might be used.

Dilatometric tests showed these new alloys to be reversible.

As a result of these tests plus other rigorous physical tests this new series of alloys was considered to have an adequate factor of safety in these respects as well as in all others.

7. *Reliability and Cost of Alloy.* These new ternary iron-nickel-chromium alloys plus small additions of other elements, can be made at a cost comparable with iron-nickel alloys containing 40 to 50 per cent nickel. Some forty heats ranging in size from 10-pound laboratory samples, melted in a small induction furnace, to 20,000-pound heats, melted in electric arc furnaces have been made up. Invariably these heats checked very closely for thermal expansion of the alloy, oxide conditions, etc. In all some 200,000 pounds of this alloy have been used. Our supplier, who makes up this alloy to our specification has informed us that it is no more difficult to hold within specifications than ordinary stainless steel, and a great deal easier to control than the iron-nickel-cobalt and iron-nickel-cobalt-chromium alloys which are also used to some extent in glass-to-metal seals.

8. *Physical and Mechanical Characteristics.* In our particular use, where the metal pins were used as radio tube contacts, it was necessary that the alloy in its final condition after processing be stiff enough to withstand stresses set up during normal tube manipulation. We were able to develop a series of alloys which was susceptible to heat treatment and whose physical characteristics could be varied over considerable limits.

In respect to normal manufacturing problems of alloy wire and sheet this material behaved similarly to other common stainless alloys. Since this phase is distinctly an alloy manufacturing problem, it will not be discussed here. It will be sufficient to say that no problems were encountered in manufacturing this new series of alloys different from those of other high nickel-iron alloys.

Development Procedure

In all some sixty-five alloys were investigated. All of these, except a few which were commercially available, were made up under closely controlled conditions in a laboratory type high frequency furnace. Each melt was approximately 10 pounds. All of this melt except one section ¼ inch in diameter and 16 inches long, which was used for physical measurements, was drawn into wire 0.050 inch in diameter, cut into pins, and sealed into glass for test purposes.

The first part of the problem of selecting a satisfactory alloy for sealing with No. 1 glass was to make a thorough study of all available alloys.

Fig. 1 shows expansivity curves for most of the major elements used in alloys for glass-to-metal seals and also some of the common alloys containing these components. This chart also shows the expansivity curve of No. 1 glass and No. 4 alloy. No. 4 alloy is one of the new series which proved to give a satisfactory match for No. 1 glass.

The curve marked Fe-Cr (Cr 30 per cent) is that of alloy No. 7 which was previously used with glass No. 3. A study of this chart shows that all of the elements shown except molybdenum and tungsten are higher in expansivity than the No. 1 glass. The exceptions are platinum which is of no practical value for this use due to high cost and chromium whose expansion has not been established definitely, mostly due to the impossibility of the preparation of ductile pure chromium. The approximate curve shown is from Desch (2) whose data are questionable due to reported anomalies in expansion between 0 and 200 degrees Cent. (32 and 390 degrees Fahr.).

Generally speaking, additions of the following elements tend to raise the expansions of known low expansion alloys, aluminum, copper, iron, nickel, chromium, silicon, manganese, beryllium, and columbium. An exception to these is the iron-chromium system.

Iron-Chromium Alloys

Since we had already had experience with No. 7 alloy (30 per cent chromium, balance iron) for sealing with No. 3 glass, our first investigation was a study of alloys of this series in order to determine whether we could lower the expansivity of these alloys below that of No. 7 by alloy modifications.

Fig. 3 shows the relative elongations of various alloys of this

type tested, and the elongation of the No. 1 glass, which we desired to match.

The curves of alloys Nos. 62 and 63 are from straight iron-chromium alloys having 12 per cent and 17½ per cent chromium respectively. This data is taken from Jones and Heselwood's (3) work on these medium chromium alloys. Curve No. 7 is that of the standard No. 446 alloy or No. 55 alloy. An inspection of these three curves shows that increasing additions of chromium to the iron-chromium system lower the expansivity of these alloys rapidly until 20 per cent chromium is reached. From 20 to 30 per cent lowers the expansion somewhat but to a much smaller degree. A special alloy, No. 48, was prepared having 40 per cent chromium, balance substantially iron. As shown in Fig. 3 the elongation of this alloy was not appreciably lower than that of alloy No. 7. From these tests it was clear that the increase in chromium content over 30 per cent in this series of alloys did not decrease the expansion of these alloys sufficiently to be of any help to us in our problem.

Alloy No. 21, Fig. 3, was a special alloy made up having 30 per cent chromium, 3 per cent molybdenum, balance iron. While the elongation is lowered somewhat it was not enough to be of any value. The same applies to alloy No. 22 which contained 30 per cent chromium, 1 per cent tungsten, balance iron. It is possible that appreciable additions in the order of 8 to 10 per cent of either tungsten or molybdenum to the 30 per cent chromium-iron alloys might have lowered the expansion of these base alloys appreciably, but due to high cost of these additions, and the extreme difficulty in cold working such alloys they were not investigated.

Alloy No. 61 is a 30 per cent chromium, 0.5 per cent carbon, balance iron alloy. In this case the addition of 0.5 per cent carbon did not lower the elongation of the base alloy appreciably.

As a result of these first series of tests we felt that the iron-chromium system of alloys would not be attractive for our particular purpose.

Iron-Nickel Alloys

Several authors have recommended iron-nickel alloys for use for sealing with lead glass. Among those who have investigated the thermal expansion of the iron-nickel system are Chevenard (4), Guillaume (5), Hidnert (6), Scott (7), and others.

Fig. 4 shows a series of expansivity curves of several of the

reversible nickel-iron alloys, also a curve on No. 1 glass. Alloys of this series between 48 and 55 per cent nickel match the glass quite closely, and show fairly strain-free seals provided the seal is annealed carefully.

A large number of tests were made with alloys of this series and No. 1 glass. In all cases during the sealing operation, an iron-nickel

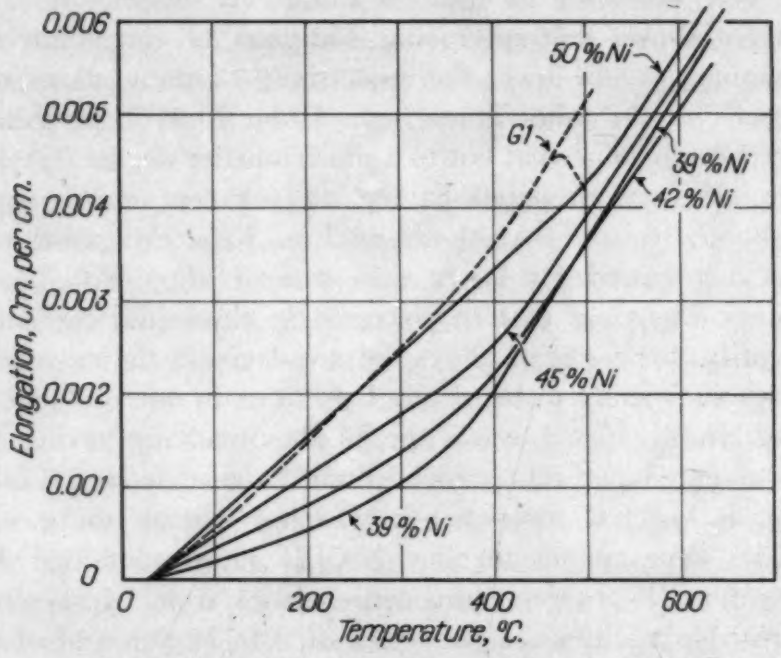


Fig. 4—Thermal Expansion Curves of Iron-Nickel Alloys.

oxide would form on the surface of the metal. This oxide was rich in nickel next to the surface of the metal and rich in iron on the outer surfaces, and tended to give a loose, scaly oxide, which while it wet the glass did not adhere to the base metal.

Seals of this type invariably leaked and we were not able to find any preoxidation treatment which would improve this condition. We were unable to form a stable oxide on the surface of these alloys which would prevent formation of an iron-rich oxide during subsequent processing.

Therefore, the iron-nickel series of alloys was rejected as inadequate for our purpose.

Iron-Nickel-Chromium-Cobalt Alloys

An effort was made to obtain a certain alloy of iron-nickel-chromium-cobalt (Fernichrome) (8) for this study. It was claimed

that this alloy would seal satisfactorily to No. 1 glass. Upon investigation we found that the alloy was not commercially available, and since due to its high cobalt constituent it would be prohibitively expensive, it was not considered for our purpose. Furthermore, we were informed by the industry that such a quarternary alloy would be exceedingly difficult to closely control from a composition standpoint, and probably from an expansion standpoint.

Iron-Nickel-Chromium Alloys

Since no commercial alloys were available which were suitable, it was necessary for us to develop one which would satisfy all conditions of use.

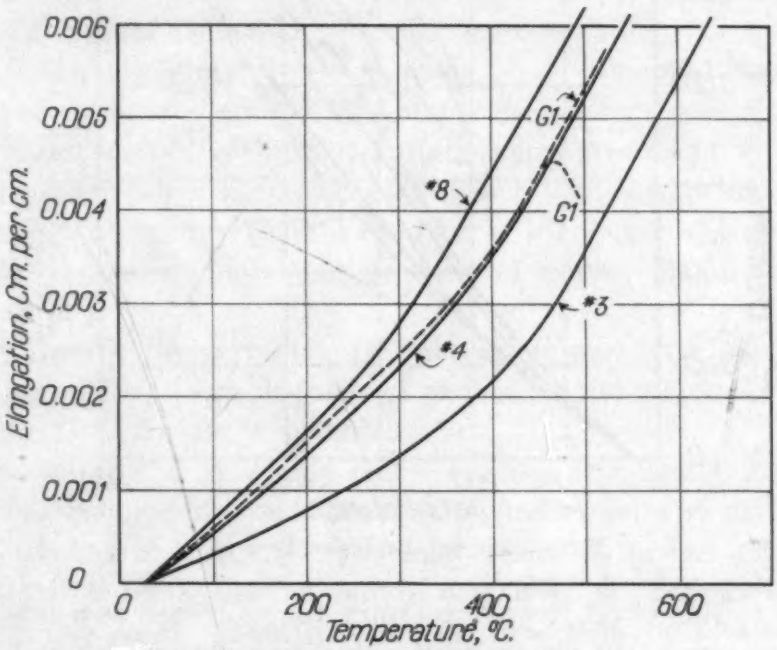


Fig. 5—Thermal Expansion Curves.

From the beginning, we felt that in order to have satisfactory seals we must have an alloy on which we could obtain an oxide which satisfied all conditions described previously in this report.

This viewpoint was arrived at after a study of all types of seals, including strain measurements, microscopic inspection of oxide layers and seals, dilatometric measurements, measurements of physical characteristics, vacuum tests, etc.

From our previous experience with No. 7 alloy (55 alloy) we felt that chromium oxide was possibly the most effective oxide layer

for any alloy for glass-to-metal seals, when used in making seals with lead glass in high production machines, where highly oxidizing flames and high temperatures were encountered.

Therefore, it seemed advisable that our alloys should contain an appreciable amount of chromium. Accordingly a study was made of the effects of the addition of chromium to the various low expansion alloy systems. It was found in all systems investigated, except the iron-chromium system, that the addition of chromium raised the expansion of that alloy appreciably.

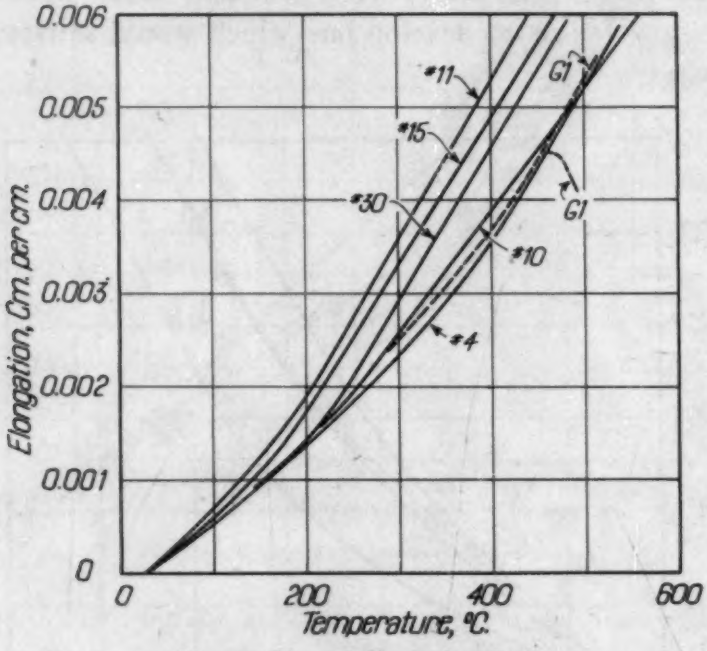


Fig. 6—Thermal Expansion Curves.

Due to this effect it was necessary for us to use as a base alloy one whose expansion was considerably lower than the No. 1 glass, and to add to it enough chromium to raise the expansion of the alloy to the proper value.

The only practical system having such low expansion characteristics was the iron-nickel system.

In Fig. 3 it is noticeable that the elongation curve of the 42 per cent nickel-iron alloy and No. 1 (G_1) glass are quite similar, except that the 42 per cent nickel-iron alloy is considerably lower in elongation. Therefore, this alloy was taken as a base and tests were made to see how much chromium was necessary to raise this alloy to the same elongation as No. 1 glass.

Fig. 5 shows the results of these tests. Alloy No. 3 is the 42 per cent nickel-iron-base alloy. No. 1 glass (G_1) is shown in the dotted curve. Two iron-nickel-chromium alloys are shown, Nos. 4 and 8. Alloy No. 4 contained 6 per cent chromium, No. 8 contained 10 per cent chromium and somewhat higher nickel. By varying the chromium content of the 42 per cent nickel-iron-base material a wide range of expansions can be obtained.

It is apparent from these curves that No. 4 alloy matches the No. 1 glass curve closely particularly throughout the annealing range of the glass, and over the temperature range to which the final glass seal would be subjected. Although these curves do not show the expansion values below room temperature, careful measurements show that the curves check closely through a temperature range from 0 to —75 degrees Cent. (32 to —105 degrees Fahr.).

Strain analysis made on seals using No. 4 alloy and No. 1 glass show no appreciable strains left in the seal after cooling to room temperature, under high production annealing processing.

This alloy is reversible, at least, over a temperature range from 1000 to —75 degrees Cent. (1830 to —105 degrees Fahr.), and dilatometric studies show that no thermal critical points occur between these points.

By varying the percentages of chromium and nickel slightly the expansion of No. 4 can be lowered so that a good match with No. 2 (Corning G-12) glass is obtained.

We found that this alloy No. 4 (42 per cent nickel, 6 per cent chromium, balance iron) contained enough chromium so that a satisfactory protective layer of Cr_2O_3 was formed by proper processing. However, this oxide did not satisfy condition No. 2 described elsewhere in this paper. That is, while the oxide was thick enough and of the proper nature to prevent subsequent formation of iron oxide it did not adhere well to the surface of the alloy.

After considerable investigation of various oxide conditions we found that it was necessary to add to No. 4 alloy or any alloy of this series a fractional amount of a constituent which would tend to make the oxide adhere tightly to the surface of the alloy. This addition was of extreme importance in alloys for this use. Various constituents were tested among those, boron, aluminum, thorium, beryllium, zirconium, strontium, carbon, titanium and others.

It is important to note that, generally speaking, additions of compound-forming elements tended to increase the adherence of the

basic chromium oxide to the surface of the metal. This is our opinion as indicated by experience.

After a study of these special additions one was selected which gave optimum results, and had the least effect on thermal expansion.

In cases where it was desirable to add a large enough percentage of these special elements to effect the expansion of the alloys, the chromium and nickel content was readjusted so that the proper ex-

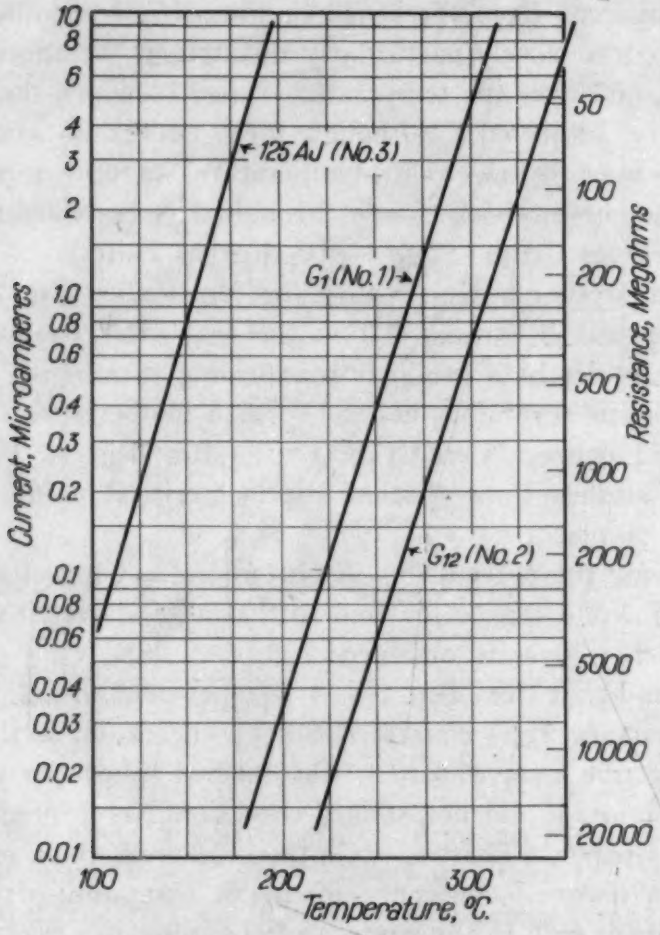


Fig. 7—Resistivity Comparative Data from Three Glasses.

pansion was attained. All of these compound-forming elements except carbon tended to increase the expansion of these iron-nickel-chromium alloys.

Our final selection of No. 4 alloy satisfied all conditions for glass-to-metal sealing outlined previously in this paper. During the development of the ternary iron-nickel-chromium No. 4 alloys, several other low expansion systems were investigated. A brief discussion of several of these will be given.

Iron-Nickel-Chromium-Carbon Alloys

Our No. 4 alloy, while entirely satisfactory for our specific use, after thorough annealing tended to become somewhat ductile. A study was made of three alloys of the No. 4 series each having different carbon contents. These alloys were subjected to various thermal treatments followed by physical testing. It was found that increasing additions of carbon raised the tensile strength and hardness of the No. 4 alloy. The following table gives hardness of these alloys after various heat treatments. All values are in Rockwell "B" numbers.

Rockwell "B" Hardness

Alloy No.	Per Cent	Per Cent	Per Cent	Cold Drawn	After Annealing at 1000 degrees Cent. in $3H_2 + N_2$ for 30 minutes	After Dilatometer Annealing
4-	42 Ni,	6 Cr,	0.07 C, bal. Fe	92	61	48
4a	42 Ni,	6 Cr,	0.22 C, bal. Fe	98	81	83
4b	42 Ni,	6 Cr,	0.52 C, bal. Fe	104	91	95
7-	(30 Cr, bal. Fe)			101	93	90

From these values it is evident that as a result of the addition of approximately 0.5 per cent carbon to the basic No. 4 alloy, the material will retain its hardness to a large extent even after thorough annealing.

Table I

Alloy No.	Alloy Composition—Per Cent by Weight—											
	Fe	C	Mn	P	S	Si	Cr	Ni	Al	Mo	W	Co
3	Bal.	.....	....	.....	.....	....	....	42.0	....	....	....	....
4	Bal.	0.04	0.29	.....	.....	0.12	6.0	42.0	....	....	....	....
7	Bal.	.....	....	.....	.....	....	30.0	....	....	....	....	....
8	Bal.	0.15	0.21	.....	.....	0.27	10.2	44.0	....	....	....	....
10	Bal.	0.055	0.10	.....	.....	0.07	0.04	42.3	....	9.60	....	....
11	Bal.	0.035	0.20	0.010	0.016	0.98	9.93	38.6	....	....	....	....
15	Bal.	0.03	0.20	.....	.....	2.74	6.10	41.2	....	....	....	....
21	Bal.	.....	....	.....	.....	....	28.0	....	....	3.0	....	....
22	Bal.	.....	....	.....	.....	....	28.0	....	....	....	1.0	....
30	Bal.	....	0.29	.....	.....	0.43	5.9	42.3	1.55	....	....	....
48	Bal.	0.076	0.52	0.014	0.022	0.52	40.3	....	....	....	....	....
61	Bal.	0.69	0.43	.....	.....	....	28.4	....	....	....	....	....
62	Bal.	.....	....	.....	.....	....	12.0	....	....	....	....	....
63	Bal.	.....	....	.....	.....	....	17.5	....	....	....	....	....

The reason for this hardening effect on an austenitic alloy of the No. 4 type is not altogether obvious since the accepted belief is that gamma iron only holds carbon as a solid solution, and as such no compounds of iron and carbon could exist. Furthermore a solid solution of carbon in gamma iron should have very little hardening effect on the alloy.

The hypothesis which we believe to be most probable is that a certain amount of delta iron-nickel-chromium is retained by the gamma iron-nickel-chromium solid solution during cooling of the melt. This delta phase has the same crystal structure as the alpha

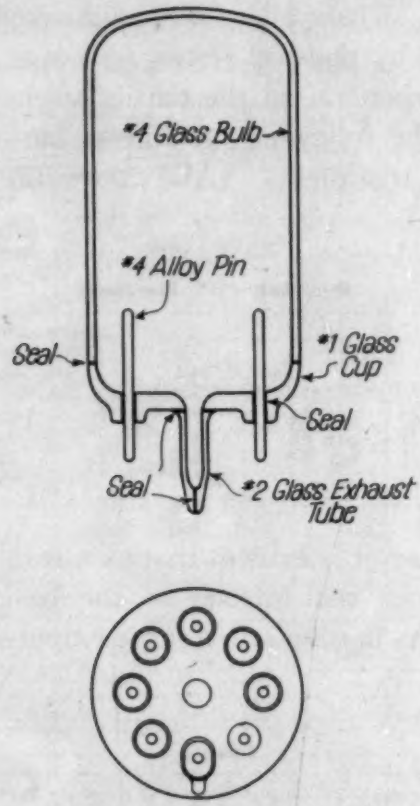


Fig. 8—Diagram of "Lock-In" Radio Tube.

and as such is capable of combining with the carbon as carbides of iron, nickel, or chromium. Microscopic investigation of these alloys has failed to substantiate this theory, since no compounds can be detected.

In any case, these tests indicate that by the addition of carbon No. 4 alloy can be hardened to a considerable degree, and this hardness can be retained even though necessary processing in the sealing operation tends to anneal the alloy.

Iron-Nickel-Silicon and Iron-Nickel-Chromium-Silicon Alloys

The addition of silicon to either the No. 4 alloy system (iron-nickel-chromium), or the 42 per cent nickel-iron system, tends to

raise the expansion of these alloys. In Fig. 6, alloys Nos. 11 and 15 are alloys of the No. 4 series having appreciable percentages of silicon. Alloy No. 15 is a standard No. 4 alloy having 6 per cent chromium, 41.2 per cent nickel, plus 2.74 per cent silicon. By comparison with alloy No. 4 the increase in expansion is seen to be appreciable. Alloy No. 11 is similar to the iron-nickel-chromium

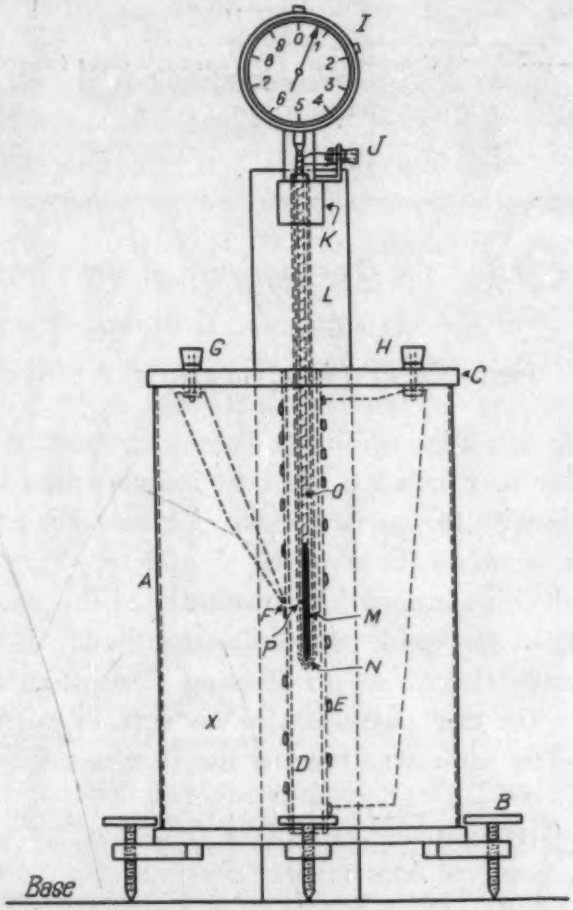


Fig. 9—Quartz Tube Dilatometer.

alloy No. 8 except that to it has been added 0.98 per cent silicon. Here again silicon increases the expansivity markedly.

Again, in the 42 per cent nickel-iron series, additions of silicon increased the elongation of the alloy. An alloy of 3 per cent silicon, 42 per cent nickel, balance iron had an elongation-temperature curve which matched No. 1 glass closely.

In all cases the addition of appreciable amounts of silicon to these alloys resulted in an inferior oxide condition. Therefore these alloys seemed unattractive for our use in glass-to-metal seals.

It is perhaps well to bring out that all of the alloys investigated contained small amounts of silicon due to melting technique. Tests showed that unless the silicon exceeded 0.25 per cent, neither the expansion nor the sealing characteristics of the alloys were appreciably affected. The same is true of manganese which up to 0.40

Table II

Glass No.	Glass Composition—Per Cent by Weight (Approx.)						
	PbO	SiO_2	MgO	K_2O	CaO	Na_2O	Al_2O_3
1	21.0	63.0	0.2	6.0	0.3	7.6	0.6
2	29.5	56.5	...	8.6	...	5.4	.....
3	18.0	66.0	2.0	...	3.0	10.0	Trace
4	....	72.8	2.8	...	4.0	20.0	.....

per cent did not affect the characteristics of the alloys to any noticeable degree.

Iron-Nickel-Molybdenum Alloys

Alloy No. 10, Fig. 6, shows the elongation of a 42 per cent nickel-iron alloy to which 9.6 per cent molybdenum has been added. Comparing this with the curve for No. 1 glass, it is evident that seals could be made between these which should be strain-free. Tests of seals made with this combination substantiated this assumption. However, an undesirable oxide condition resulted. Furthermore, the high cost of molybdenum as an alloying element prohibited the use of these alloys for our purpose and no further work was done on these alloys. The same was true of the iron-nickel-tungsten system.

Iron-Nickel-Chromium-Aluminum System and Iron-Nickel-Aluminum System

A number of iron-nickel-chromium-aluminum and iron-nickel-aluminum alloys were investigated. One of these is alloy No. 30, shown in Fig. 6.

As a result of these tests it was found that additions of aluminum to these alloys increased their expansivities in all cases, the degree of increase depending upon the proportion of aluminum.

Since it is considered very difficult to process alloys of this type, containing appreciable percentages of aluminum due to cracks, fissures, etc. in the material, these alloys were not considered attractive for our use.

Tables I and II show the compositions of the alloys and glasses referred to in the text.

Fig. 9 shows a sketch of precision dilatometer used in making elongation measurements. This instrument is of the standard concentric quartz tube type, modified somewhat to increase accuracy.

Conclusion

A new series of iron-nickel-chromium alloys (plus other small additions) have been developed which have characteristics making them particularly suitable for vacuum-tight glass-to-metal seals. By varying the principal constituents of these alloys, coefficients of expansions ranging from 70 x 10^{-7} to 120 x 10^{-7} per degree Cent. can be obtained. Due to the great inherent strength of the bond between these metals and their associated glasses, they should be well adapted for seals to glass where large mechanical stresses are encountered. These alloys are low in cost and can be made successfully by standard metallurgical methods. This series of alloys have excellent stainless properties.

At this date of writing, patents are pending on this series of alloys.

Bibliography

1. Eldred, U. S. Patent 1,140,136.
2. J. Desch, *Zeitschrift für Physik,* Vol. 5, 1921, p. 173.
3. J. A. Jones and W. C. Haselwood, *Journal,* Iron and Steel Institute, Vol. 137, 1938, p. 361-382.
4. P. Chevenard, *Revue de Metallurgie Me'm.,* Vol. 11, 1914, p. 841-862.
5. C. R. Guillaume, *Academy of Sciences,* Paris, Vol. 124, 1897, p. 176-179.
6. Circular of the National Bureau of Standards, No. 58, 1923.
7. H. Scott, "Expansion Characteristics of Low-Expansion Nickel Steels," Transactions, American Society for Steel Treating, Vol. 13, 1928, p. 829.
8. A. W. Hull and E. E. Burger, *Physics,* Vol. 5, 1934, p. 384-405.

THE EFFECT OF STRAIN RATE UPON THE TENSILE IMPACT STRENGTH OF SOME METALS

By E. R. Parker and C. Ferguson

Abstract

High velocity tension impact tests were conducted on a number of metals and alloys. The energy absorbed during rupture and the elongation and reduction of area of the fractured bars are reported. Most materials tested absorbed more energy at higher impact velocities. However, there were exceptions which serve as warnings against drawing general conclusions about the effect of velocity on impact strength.

A STUDY of the literature (1) through (10)[1] reveals that there is considerable confusion in the field of impact testing, particularly in the interpretation of test results and the relation of the impact strength to other physical properties. Recently, however, some noteworthy studies (see bibliography at end of paper) have been made which have aided greatly in putting impact testing on an analytical basis. The investigation reported herein is presented with the hope that it will add another link to the chain of evidence which will some day reveal the secrets which now lie hidden in the mysteries veiling impact failures.

The object of the investigation was to determine how much energy metals could absorb at high strain rates. Some tests were also conducted to determine the effect of specimen design on the energy absorbed during fracture. All tests were of the tensile type, made on bars of the designs shown in Fig. 1. The letters assigned to the various specimens shown in this figure are used throughout the text to indicate the type of bar used for the tests. The static, or "zero strain rate" tests (strain rate approximately 4×10^{-4} inches per inch per second), were made on a 20,000 pound screw-driven tensile machine by measuring the load and strain throughout the test. The impact, or "rapid strain rate," tests were made on the variable-velocity impact machine shown in Fig. 2. The construc-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. The authors, E. R. Parker and C. Ferguson, are associated with the research laboratory, General Electric Company, Schenectady, N. Y. Manuscript received June 19, 1941.

tion and operation of this machine have been adequately described elsewhere (4). It is sufficient to state here that the machine consists of a rotating flywheel (the source of energy required for breaking the test bar), a pendulum mounted independently on the flywheel shaft, a speed indicator, and a device for measuring the swing of the pendulum when the specimen is broken. A retractable hammer is held in position in the flywheel until the desired velocity

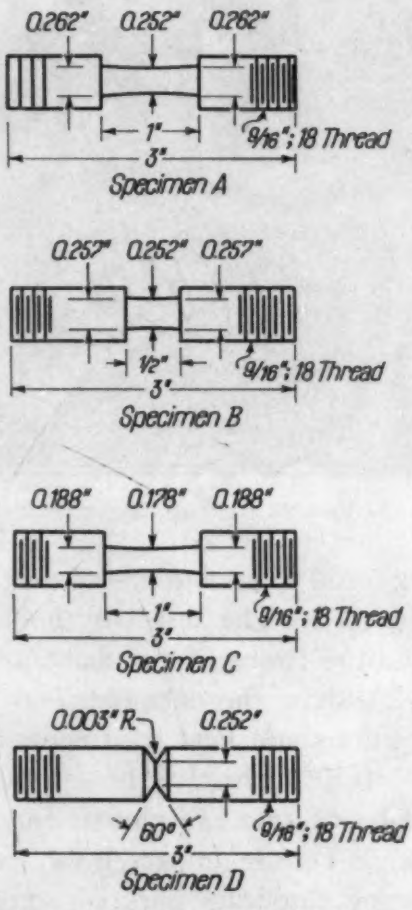


Fig. 1—Tensile Test Bars. Used in Making Tests Described in This Paper.

is reached. At this instant, a trip mechanism releases the hammer, which moves outward against suitable stops. The hammer strikes a tup screwed on the free end of the bar, and fracture of the specimen results. The force applied to the free end of the bar by the hammer is transmitted to the other end of the bar, which is screwed into the pendulum, causing the pendulum to swing in the direction of the blow. Knowing the speed of the flywheel, the swing of the pendulum, the constants of the machine, and using the laws of

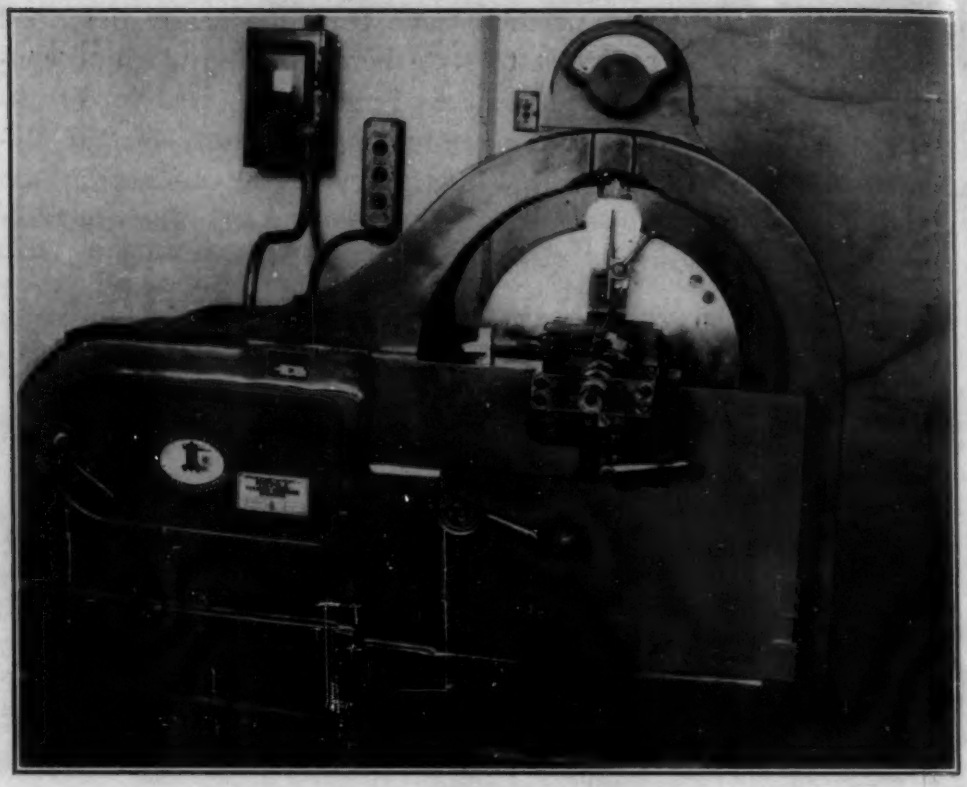


Fig. 2—Variable Velocity Impact Machine.

conservation of energy and momentum, the energy absorbed by the bar can be calculated (4). The test bar, holder, and tup can be seen in Fig. 2 lying on the frame of the machine.

Figs. 3 through 21 show the data obtained with several metals for which the compositions and heat treatments are shown in Table I. The energy absorbed during rupture and the corresponding elongation and reduction of area are plotted for various strain rates (or impact velocities). Tensile impact tests were also made with a Charpy machine using duplicate bars of some of the materials. The results thus obtained are plotted with the other impact results, but they are marked "Charpy tests" to distinguish them. Certain errors in measurements must be considered in an analysis of the results. The tup and hammer deform somewhat with each test, particularly at high impact velocities. Also, there was noticeable deformation in the threaded ends of some of the test bars. Impact energies are not plotted for the tests showing noticeable deformation in the threads because such energies do not represent the impact strength of the material within the gage length. Probably

Table I

Alloy	Nominal Composition in Per Cent														Heat Treatment	Static Tensile Strength of Specimen A, Psi.
	Al	C	Cr	Cu	Fe	Mg	Mn	Ni	O	P	Pb	S	Si	Zn		
High Purity Aluminum	99.99	....	....	....	....	....	....	....	....	....	....	....	....	....	2 Hours 250° C., air-cooled	9,200
Duralumin (17 S-T)	94.	....	....	4.	1.	0.5	0.5	....	....	....	....	....	....	....	Water quenched from 500° C.	56,000
Brass (unannealed)	....	....	....	62.	....	....	....	....	....	....	3.	....	....	35.	Tested as drawn	54,000
Brass (annealed)	....	....	....	62.	....	....	....	....	....	....	3.	....	....	35.	1 Hour 400° C., air-cooled	51,500
OFHC Copper	....	....	....	99.98 (See ASM Handbook for typical analysis)											1 Hour 850° C., furnace-cooled	29,500
Tough Pitch Copper	....	....	....	99.95	....	....	....	....	0.035	....	....	....	....	....	1 Hour 400° C., furnace-cooled	31,000
Lead	....	....	....	....	....	....	....	....	....	....	99.99	....	....	....	1 Hour 200° C., air-cooled	1,950
Nickel	....	0.1	....	0.1	0.15	....	0.20	99.4	....	....	....	0.005	0.05	....	1 Hour 850° C., air-cooled	72,000
Cold-Rolled Steel (S.A.E. 1112)	....	0.12	....	....	Bal.	....	0.75	....	....	0.10	....	0.15	....	....	Tested as-rolled	91,000
S.A.E. 1040	....	0.40	....	....	....	....	0.75	....	....	0.04	....	0.04	....	....	1 Hour 840° C., furnace-cooled	84,000
S.A.E. 1040	....	0.40	....	....	....	....	0.75	....	....	0.04	....	0.04	....	....	1 Hour 840° C., air-cooled 1 Hour 650° C., air-cooled	87,000
18-8 Stainless Steel	....	....	18.	....	74.	....	....	8.	....	....	....	....	....	....	Hot-rolled	120,000

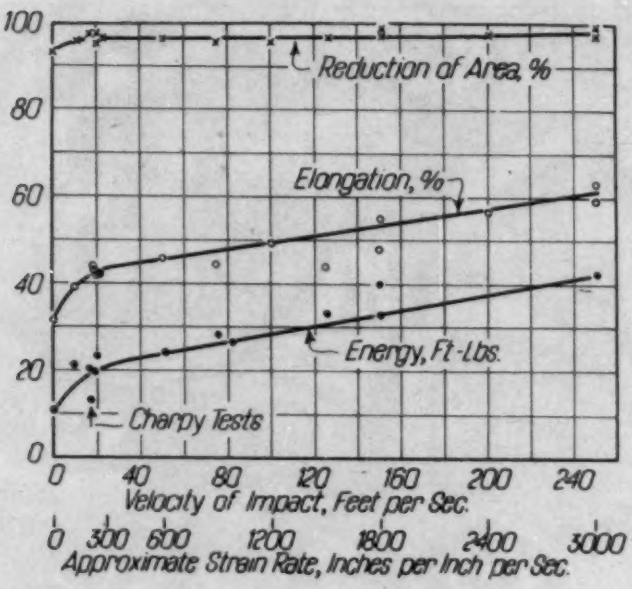


Fig. 3—High Velocity Tension Impact, Aluminum, Specimen A.

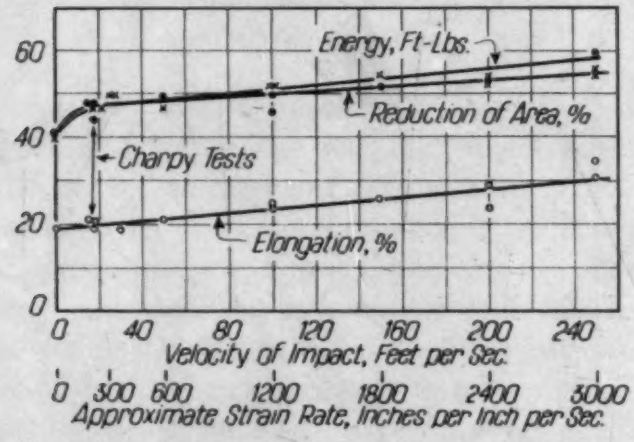


Fig. 4—High Velocity Tension Impact, Duralumin, Specimen A.

unobservable deformation occurred in the threads of some of the other bars, causing the energies to read somewhat high. The energy absorbed by the tup, the hammer, and possibly the threads of some of the test bars is included in the reported impact energy.

With the exception of the 18-8 stainless steel, less energy was absorbed during the static test than in the dynamic tests; and, in general, the ductility increased continuously as the speed of the

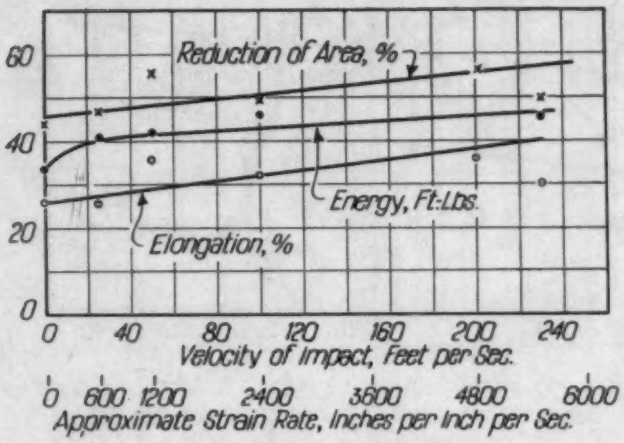


Fig. 5—High Velocity Tension Impact, Duralumin, Specimen B.

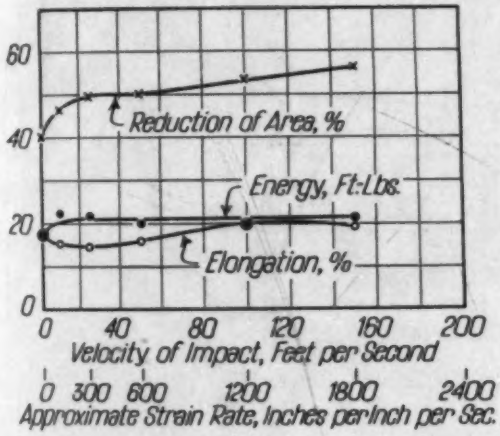


Fig. 6—High Velocity Tension Impact, Duralumin, Specimen C.

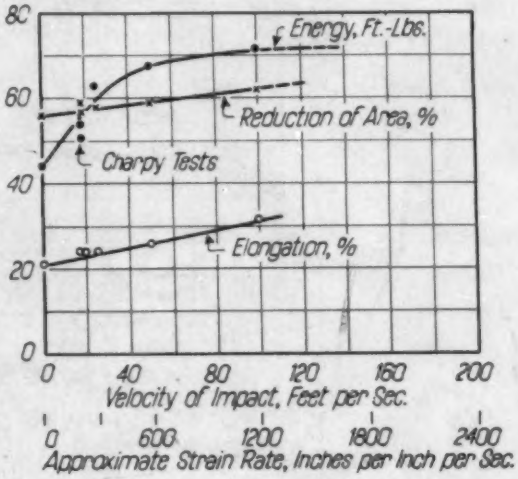


Fig. 7—High Velocity Tension Impact, Brass, Unannealed, Specimen A.

test increased. From an examination of the results, it is apparent that no general conclusions can be drawn concerning the effect of strain rate on such properties as impact strength, elongation, and reduction of area.

The volumes of bar B and bar C are equal to half the volume of bar A (see Fig. 1), yet there is no apparent correlation of the energies absorbed by the different types of bars of the same material. One interesting feature of the results is the correlation of static and dynamic properties. The elongation-strain rate curves and the reduction of area-strain rate curves are, in most cases, essentially straight lines, starting at the values obtained in the static

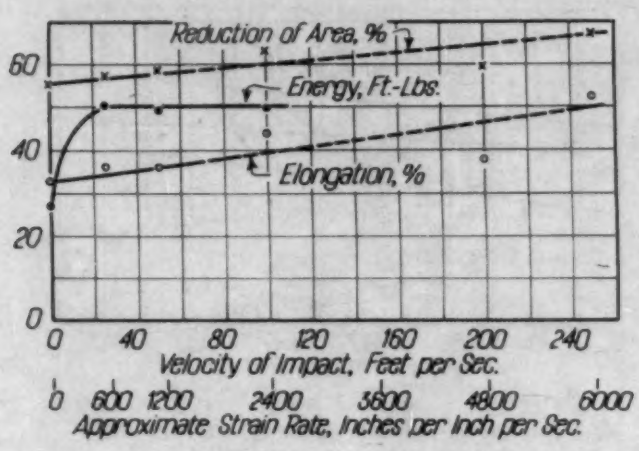


Fig. 8—High Velocity Tension Impact, Brass, Unannealed, Specimen B.

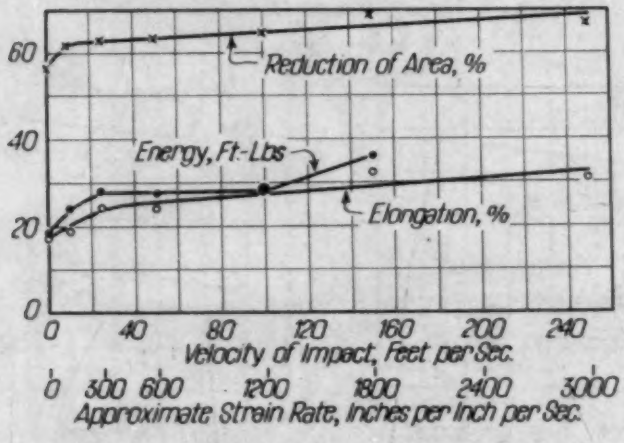


Fig. 9—High Velocity Tension Impact, Brass, Unannealed, Specimen C.

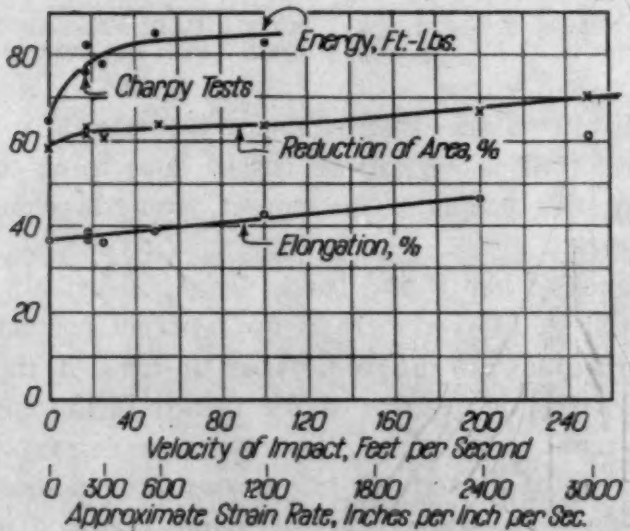


Fig. 10—High Velocity Tension Impact, Brass, Annealed, Specimen A.

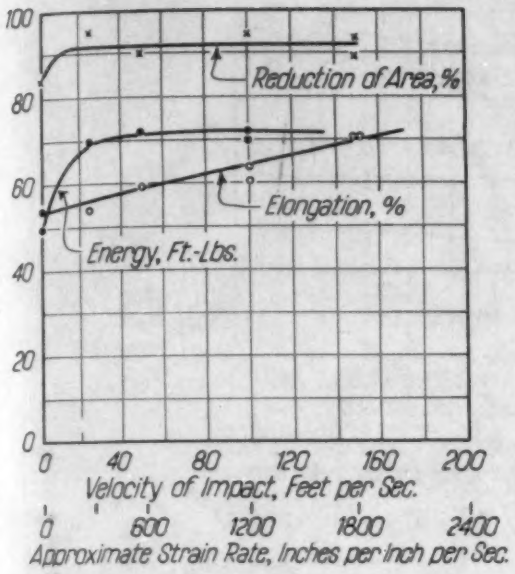

Reduction of Area, %
Elongation, %
Energy, Ft.-Lbs.
Velocity of Impact, Feet per Sec.
Approximate Strain Rate, Inches per Inch per Sec.

Fig. 11—High Velocity Tension Impact, OFHC Copper, Specimen A.

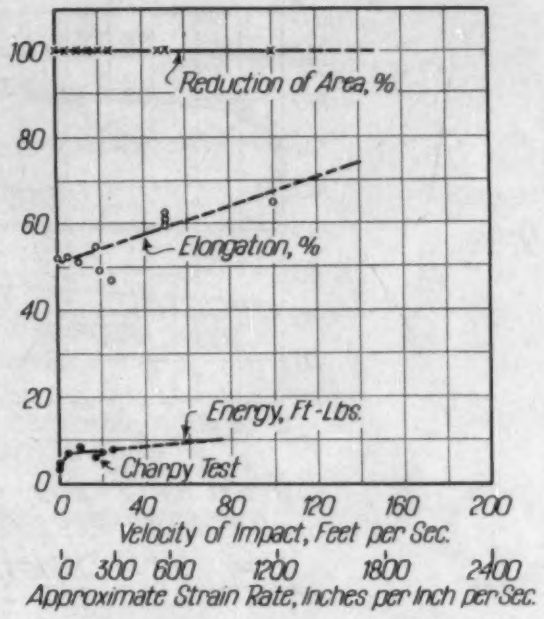

Reduction of Area, %
Elongation, %
Energy, Ft-Lbs.
Charpy Test
Velocity of Impact, Feet per Sec.
Approximate Strain Rate, Inches per Inch per Sec.

Fig. 13—High Velocity Tension Impact, Lead, Specimen A.

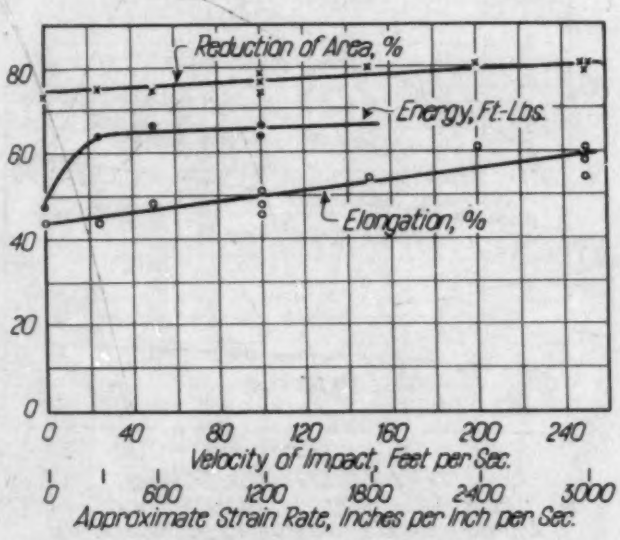

Reduction of Area, %
Energy, Ft.-Lbs.
Elongation, %
Velocity of Impact, Feet per Sec.
Approximate Strain Rate, Inches per Inch per Sec.

Fig. 12—High Velocity Tension Impact, Tough Pitch Copper, Specimen A.

tests and increasing as the velocity of impact increases. For most of the metals tested, the energies obtained in the static tests fall on smooth curves which rise rapidly at low strain rates and then less rapidly as the strain rate increases further. There are, of course, exceptions such as the 18-8 stainless steel, the S.A.E. 1040 steel, the

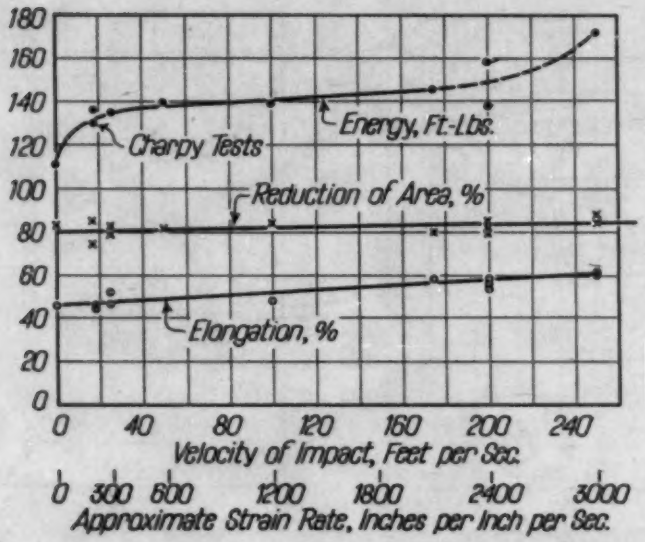


Fig. 14—High Velocity Tension Impact, Nickel, Specimen A.

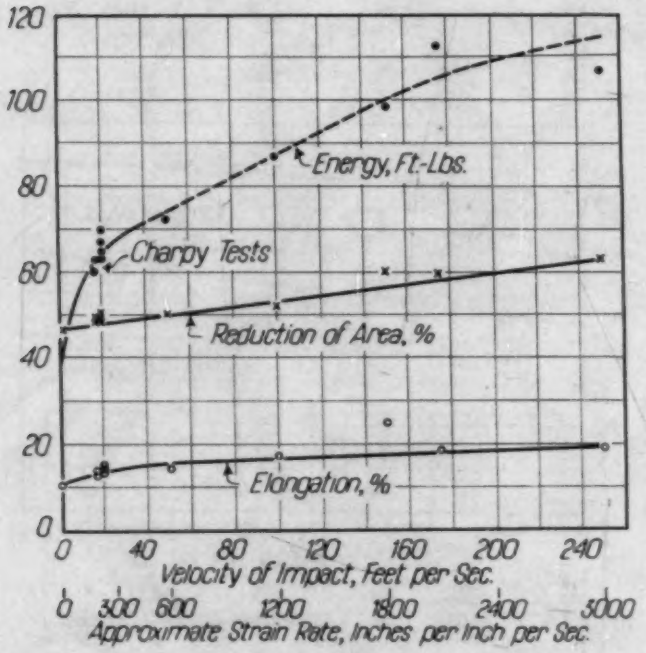


Fig. 15—High Velocity Tension Impact, Cold-Rolled Steel, Specimen A.

½-inch gage length cold-rolled steel, and the notched cold-rolled steel. Data for the notched cold-rolled steel do not fall on a smooth curve, but evidently less energy is absorbed when notched bars of this material are broken at high strain rates. The 18-8 stainless steel gives a very peculiar but repeatable energy-strain rate curve.

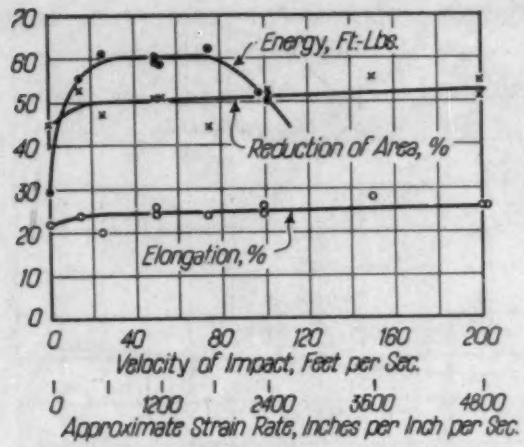

Energy, Ft.-Lbs.
Reduction of Area, %
Elongation, %
Velocity of Impact, Feet per Sec.
Approximate Strain Rate, Inches per Inch per Sec.

Fig. 16—High Velocity Tension Impact, Cold-Rolled Steel, Specimen B.

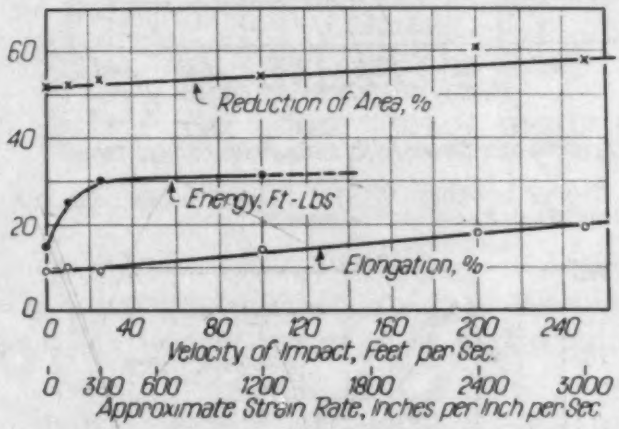

Reduction of Area, %
Energy, Ft-Lbs
Elongation, %
Velocity of Impact, Feet per Sec.
Approximate Strain Rate, Inches per Inch per Sec.

Fig. 17—High Velocity Tension Impact, Cold-Rolled Steel, Specimen C.

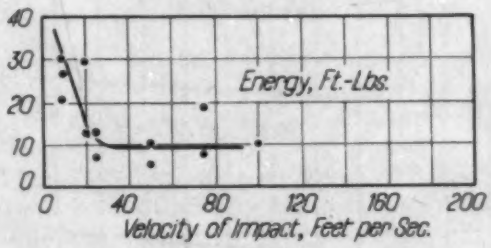


Fig. 18—High Velocity Tension Impact, Cold-Rolled Steel, Specimen D.

The energy decreases at first, then rises rapidly to a maximum, then drops slowly to a second minimum, followed by a gradual rise. The elongation and reduction of area curves drop rapidly at first to a minimum followed by a continuous slow increase. Curves for the S.A.E. 1040 steel are also unusual. The energy curve rises rapidly

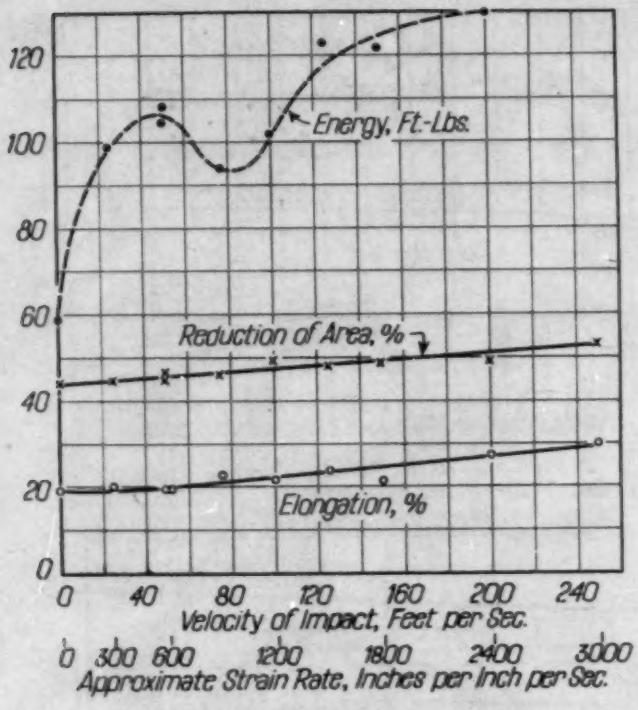


Fig. 19—High Velocity Tension Impact, S.A.E. 1040 Steel Annealed, Specimen A.

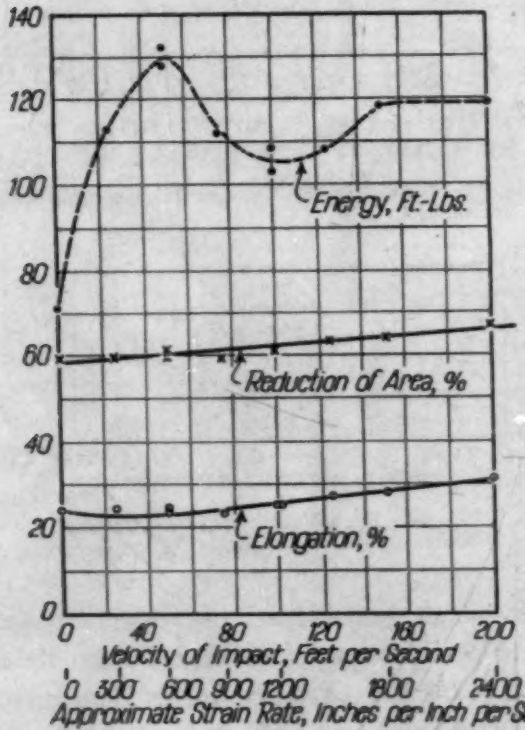


Fig. 20—High Velocity Tension Impact, S.A.E. 1040 Steel Normalized & Drawn, Specimen A.

from the zero strain-rate values to a maximum, followed by a sharp drop to a minimum, then gradually rises.

In a preliminary investigation of this sort, it seems advisable to investigate a large variety of metals rather than to make a com-

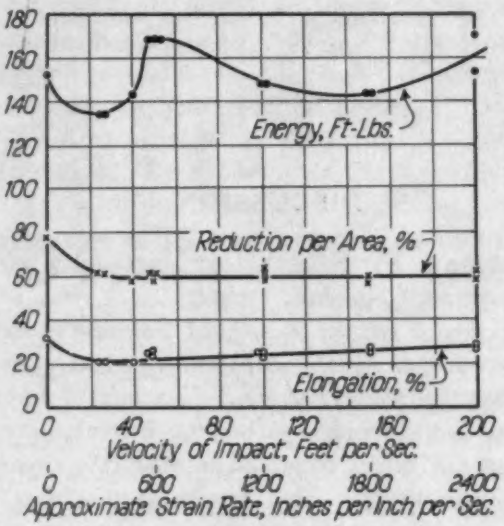


Fig. 21—High Velocity Tension Impact, 18-8 Stainless Steel, Specimen A.

prehensive study of one or two materials. The unusual results obtained with 18-8 stainless steel serve as a warning against drawing general conclusions from a few tests or extrapolating results into unexplored regions. Even with pure metals, caution should be exercised in drawing general conclusions since it has been shown that the energy absorbed by zinc is less at high strain rates (8).

Bibliography

1. Symposium on Impact Testing of Materials, *Proceedings,* American Society for Testing Materials, Vol. 22, Pt. II, 1922.
2. "Notched Bar Testing of Steel," METALS HANDBOOK, American Society for Metals, 1939, p. 671-677.
3. H. C. Mann, "The Relation Between Tension Static and Dynamic Tests," *Proceedings,* American Society for Testing Materials, Vol. 35, Pt. II, 1935, p. 323-340.
4. H. C. Mann, "High-Velocity Tension-Impact Tests," *Proceedings,* American Society for Testing Materials, Vol. 36, Pt. II, 1936, p. 85-109.
5. H. C. Mann, "A Fundamental Study of the Design of Impact Test Specimens," *Proceedings,* American Society for Testing Materials, Vol. 37, Pt. II, 1937, p. 102-118.
6. G. F. Jenks, "Application of Tension-Impact Tests," *Transactions,* American Society of Mechanical Engineers, Vol. 59, No. 5, 1937, p. 313-318.
7. D. S. Clark and G. Datwyler, "Stress-Strain Relations Under Tension Impact Loading," *Proceedings,* American Society for Testing Materials, Vol. 38, Pt. II, 1938, p. 98-111.

8. G. Welter and S. Morski, "Dynamic Tensile Properties and Stress-Strain Diagrams of Some Constructional Materials," *Journal,* Institute of Metals, April 1940, p. 97-107.
9. M. Manjoine and A. Nadai, "High-Speed Tension Tests at Elevated Temperatures," *Proceedings,* American Society for Testing Materials, Vol. 40, 1940, p. 823-839.
10. D. W. Ginns, "The Mechanical Properties of Some Metals and Alloys Broken at Ultra High Speeds," *Journal,* Institute of Metals, Vol. LXI, No. 2, 1937, p. 61-78.

DISCUSSION

Written Discussion: By S. L. Hoyt, metallurgical research advisor, Battelle Memorial Institute, Columbus, Ohio.

This paper is evidence of the desire of engineers and metallurgists to learn more of the behavior of metals when deformed at high velocity. At this stage it seems well worthwhile to examine a variety of metals and to include more than one size of test specimen, to become better oriented in the field.

The curves indicate a fairly common pattern of increasing ductility with increase of deformation velocity. This agrees with earlier work though the present investigation covers a greater range of velocities than is usual. The 18-8 sample is an exception to this rule and straight chromium steels are also held to be less ductile in impact and to show rather pronounced temperature sensitivity. As in the case of notch behavior, temperature is an important variable and it is suggested that the authors would do well to include it in their own work.

The general pattern of the effect of velocity on the energy absorption tends to be about the same as that just discussed though with some important exceptions or at least anomalies. Determination of the energy values brings up what is perhaps the most serious objection to the equipment or method used in this study, failure to determine the stresses generated in the test bars. Apparently the authors secured an energy reading from the swing of their pendulum which they assumed approximated the integrated value of stress times strain for the test bar. The method is simple but nevertheless leaves room for serious doubt as to how much energy was absorbed in actually deforming the test bar and how much was due to other or extraneous sources. It is only fair to state that the curves reproduced do not indicate obvious errors. In this connection Dr. Nadai in his talk to the University of Pennsylvania conference on the deformation of metals described a method used at the Westinghouse laboratories which gives the complete stress-strain relationships. I also understand that Dr. Clark in his investigations at the California Institute of Technology has gone to higher speeds than those reported in 1938 and also obtains complete stress-strain diagrams. By giving measures of the stress it is believed that the results are much more trustworthy than those obtained by the pendulum device. For example, the curves of Figs. 19, 20, and 21 show decreasing energy values for increasing elongation. Such effects could be understood or accepted only in case it was known that the stress

values decreased over the same range. The curve of Fig. 18 raises some interesting points. The actual energy values at low velocity seem to be relatively high for a notched specimen. Also the energy value drops to a low level rather quickly and this suggests that the notch of Specimen D gives a rather critical notch effect for this cold-rolled steel. While this is understandable and has been found before, it would be interesting to know if this drop in energy is actually due to that cause. Without some such amplification Fig. 18 stands as an isolated case and one might be misled to accept it as indicating the general effect of velocity on notch toughness. Usually notch toughness values have been found to increase with velocity.

Written Discussion: By Donald S. Clark, assistant professor of mechanical engineering, California Institute of Technology, Pasadena, Cal.

It is indeed gratifying to see the increasing interest in tension impact testing and to know that others are endeavoring to find a basic understanding of the impact problem. To many, the impact test still means the Charpy or Izod tests and this impression will remain until a sufficient number of papers of the type presented by the authors have appeared. A mechanical test has been defined as any test in which the variables are controlled and the results are quantitatively measured. Hence, in order for the results to be of real significance, all the variables must be separated and controlled. Furthermore, the effect of varying each of these independent variables must be studied by measuring the changes of the fundamental characteristics of the material. It is of course, necessary to compare the laboratory test results with service tests. This paper reports the effect of velocity on the energy-absorbing capacity, the per cent elongation and the reduction of area for several materials. Energy is an integral value of a force-distance relation, and hence, does not give the complete picture of the fundamental effect of velocity on the behavior of the material. This is not meant as a criticism of this work, but I wish to call attention to a point which may be of significance. We have already found that increasing the rate of strain brings about marked changes in yield point and ultimate strength in a manner which cannot be established by determining the total energy absorbed. So far, the fundamental significance of these changes has not been discovered. However, the continued effort on this problem by more people will, we hope, lead to a better understanding of the relation of rate of strain to mechanical properties. The authors should be encouraged to continue their investigation.

The investigations being made at California Institute of Technology involve the measurement of stress and strain during tension impact within the velocity range of 0 to about 200 feet per second. We have investigated a rather large number of materials, some of which are similar to those reported in this paper. Our specimens are 0.200 inch in diameter over a gage length of 1 inch. In spite of the difference in specimen dimensions and probable differences in the composition and structural condition of the materials, our results are similar to those shown by the authors. Our results indicate an increase of energy for cold-rolled S.A.E. 1112 steel to a maximum at about 75 feet per second and then a slight decrease up to 160 feet per second. In most cases our results verify those of the authors with respect to the linearity of the elongation and reduction of area vs. velocity relations.

Our results for 18-8 stainless steel are very similar to those reported by the authors. The total energy decreases at first and then increases, reaching a maximum at a velocity of about 60 feet per second. The general trend of elongation and reduction of area reported for this alloy are checked by our work.

The results reported by the authors seem to be at variance with those obtained by the original investigators[1] who developed the machine employed. The curves presented in this paper do not show the marked decrease of energy with increasing velocity. Several authorities have questioned the correctness of the method of measuring energy with the mechanism used in this machine. It would be of great interest to know what changes, if any, have been made in the machine which have made it possible to obtain these more logical results.

The marked decrease of energy with increasing velocity obtained with the notched specimen (Fig. 18) seems to be logical. I should like to know if the authors have obtained any results with different notch depths and different notch shapes.

Written Discussion: By A. Nadai, consulting mechanical engineer, Westinghouse Research Laboratories, East Pittsburgh, Pa.

The authors have made a large number of rapid tension tests using the high velocity tension impact machine which was developed by H. C. Mann. It can be noted from their various curve sheets that in most of the observed cases the energy to break a tension specimen continuously increases with the speed of deformation; however, they point to a few exceptions such as can be seen in Figs. 19 and 20 referring to high velocity tension tests with S.A.E. 1040 steel (also stainless steel shows a similar effect). In these cases the energy first increases then decreases and again increases with the rate of stretching. It would have been valuable if the authors could have advanced some explanation for these remarkable fluctuations of the impact energies. It is noted that in none of the tests for smooth (not notched) tension specimens reported by the authors in their paper was there an indication of the sharp decrease of the energy which was reported in the early experiments of Mr. Mann.

As long as the energy is chosen as the quantity to be measured during the pure plastic deformation of the cylindrical gage lengths of a tension bar it has a certain value to record this energy. Tension tests made under high speeds of deformation at room temperature have shown recently that the plastic elongation at fracture increases only slightly with the speed of stretching. Assuming that the elongation would not essentially change with the speed of deformation the energy can be considered as a certain indication of the mean value of the yield stresses in the tensile stress-strain diagram. The experiments of the authors then indicate that in accordance with other experiments the mean value of the yield stress increases with the speed of stretching with the above mentioned few exceptions. However, the authors point out themselves in their paper that energy losses were observed through the permanent deformation of the threads and of the adjoining parts of the machine. No attempt was made by the authors to separate these amounts from the overall energies which they were able to record. Further attention should in addition

[1] H. C. Mann, "High Velocity Tension-Impact Tests," *Proceedings*, American Society for Testing Materials, Vol. 36, 1936, Part II, p. 85.

be called to the elastic energies involved. The elastic and the kinetic energy of the longitudinal oscillations of the test bar may become quite considerable under very high velocities of impact testing. It is well known that the impact problem is complicated by two facts: (a) that at high impact velocities no equilibrium exists between the forces stretching the bar; (b) that in the case of a notched bar test (such as specimen d) nonuniformity of the stress distribution near the notch makes it practically impossible to draw any concrete conclusions from such tests. The phenomena connected with a very rapid change in load in a notched specimen leading to fracture are so complicated that it is scarcely possible to speak of an "impact strength" of a material to be determined by breaking notched specimens.

As long as the stress-strain curve is not recorded on the tension specimen itself it seems that it is not possible to state something more definite by only recording the total energy as a function of the speed of deformation because of

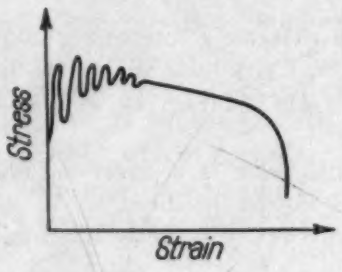


Fig. 1A

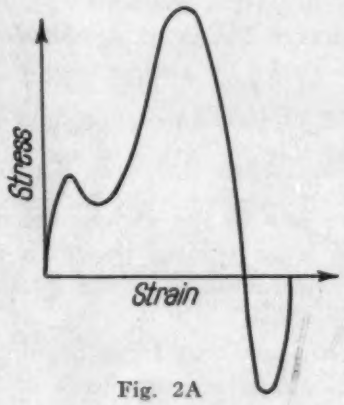


Fig. 2A

the various losses of energy which are connected with a suddenly or very rapidly increasing load. It may be of interest in connection with these tests to mention that in a series of high speed tension tests made at the Westinghouse Research Laboratories recently[2] our experience led us to believe—at least under the conditions which were given in our high speed machine—that it was not possible to record undisturbed stress-strain curves when the strain rates were much larger than 1000 per second. Stress-strain diagrams at still higher rates were so seriously disturbed through the dynamic effects of the superposed longitudinal oscillations of the force measuring system including the test specimen that it was practically impossible to speak of a diagram when the speed rates were much higher than 1000 per second. The two figures, Figs. 1A and 2A, may illustrate this. In one of them it can be noted that many oscillations appear so that the time of one oscillation is a small fraction of the time of testing. This is the case for slower rates of deformation; how-

[2]M. J. Manjoine and A. Nadai, "High Speed Tension Tests at Elevated Temperatures —Part I," *Proceedings*, American Society for Testing Materials, Vol. 40, 1940, Parts II and III; *Journal of Applied Mechanics*, American Society of Mechanical Engineers, June, 1941.

ever, if the speed of deformation increases sufficiently the diagrams were violently disturbed as indicated by Fig. 2A. One or two waves spread over the entire length of the diagram. The authors used specimens of a similar form than the ones used in the Pittsburgh machine. Since also the energy (or force) measuring system was a very rigid one, one could possibly assume that the frequencies of the elastic oscillations were of a similar order. The authors recorded test curves for a strain rate of 3000 per second. Assuming an elongation of 25 per cent and a gage length of the specimen of 1 inch, this would correspond to a testing time of one twelve-thousandth of a second for their fastest tests. Under such high rates of stretching it is suspected that the stress-strain curves if they would have been recorded would have shown disturbances through the longitudinal oscillations. Since during these latter kinetic and elastic energy are exchanged in rapid succession in the test bar and in the adjoining parts of the machine which energies are dissipated through damping, recording of values of the true energy for plastic deformation must become difficult.

Oral Discussion

A. V. DEFOREST:[3] This matter is an extremely interesting one, especially in the field of instrumentation, and as Dr. Clark said in his discussion, it is highly desirable to have a whole stress-strain diagram as well as the energy absorption.

As we saw in the various discussions, there is a question, and has been ever since Mann devised this high speed impact machine, as to whether the method of measurement of the total energy really is or is not free of instrumental difficulties.

The only way that I can possibly guess that it is going to be solved is to have simultaneous measurements of the stress-strain relationship at the same time as the energy measurement on the same machine.

Dr. Nadai's machine solved the problem in a very neat way, and his diagrams are the most elegant that have yet come out.

Dr. Nadai has mentioned the very great difficulty involved in high speed impact testing and simultaneous recording of the stress-strain diagram. The system, including the test piece, is full of longitudinal vibrations at the sonic frequency of the whole system, including the test piece, the loading tup, and the support, so that it is a very complicated system which produces these longitudinal vibrations simultaneously with the stress of the test specimen, and the stretch of the test specimen does not damp out the longitudinal vibrations as much as one would expect.

Even in Dr. Nadai's copper which one would think a most efficient energy absorber, at high frequency there appeared to be longitudinal vibrations at the same time.

Several years ago, we had the opportunity of making longitudinal strain measurements on Mann's machine, and came to the conclusion that there was so much vibration present in the specimens that we were measuring, at any rate, that it was hopeless to try to unscramble the discrepancy of the

[3]Professor of mechanical engineering, Massachusetts Institute of Technology, Cambridge, Mass.

energy value from the measurements made on that machine with that type of specimen. However, I very much hope that the General Electric Company and Mr. Parker will be able to solve that problem. Certainly at the lower speeds it would be perfectly simple. At the higher speeds, we will wait and see what turns out.

Authors' Reply

I want to thank the gentlemen for their discussions of this paper and to point out that we realize the shortcomings of test results that we have presented and that we are taking steps now to remedy those shortcomings. This paper is in the nature of a progress report rather than a complete presentation of data.

The measurement of energy alone, of course, is not sufficient to completely define the conditions of test or to tell us the fundamental properties of the material. At the present time, we are building oscillographic equipment with which we hope to measure load as a function of time and extension as a function of time for each test bar. Eventually we hope to record dynamic stress-strain curves at all speeds. Simultaneous measurements of energy using the present methods of measurement and calculation will be made for comparison.

It is of some interest, though, to point out that Professor Clark had made energy measurements by integrating force and extension throughout the dynamic impact tests which he had conducted. In his discussion he says that he obtained with materials similar to ours energy versus impact velocity curves of the same general type, particularly with 18-8 stainless steel, which exhibits the peculiar curve of decreasing energy at low impact velocities, followed by an increase which goes through a maximum, and then to a minimum again, followed by a steady increase at higher velocities.

Dr. Hoyt and the other gentlemen are correct in stating that there are certain errors inherent in this method of testing which should be pointed out. They are pointed out to some extent in the paper. These errors are due, mainly, to the deformation which occurs in the metal parts of the test bar and machine outside of the gage length of the test specimen, such as the deformation of the hammer during the impact test, the deformation which occurs in the tup, and the deformation which occurs in the threaded portion of the test bar. It is interesting to note, however, that tension impact tests on identical bars made in the Charpy machine absorbed essentially the same energy as bars broken in the variable velocity machine. Thus errors in energy measurement are apparently of the same order of magnitude in the two machines. In any test where there was an obvious error, such as deformation in the threaded portion of the test bar, we did not report the results.

Professor Clark asked if there was any difference between our machine and the one used by Mann. To the best of our knowledge, the machine we used is built like Mann's (the only changes made were minor ones such as in the frame, housing, etc.). The energy was calculated using the method employed by Mann.

Concerning the notched specimens, we have little information to offer. The only tests made on notched bars were reported in the paper.

SOME PROPERTIES OF SINTERED AND HOT-PRESSED COPPER-ZINC POWDER COMPACTS

By Claus G. Goetzel

Abstract

Binary brasses with different percentages of zinc have been prepared from metallic powders. Their microstructure, density, hardness and compressive properties have been studied. The effect of certain basic factors upon these properties, such as composition and type of raw material used, or the molding pressure employed, has been investigated. A comparison has been made of the properties of sintered compacts with those of hot-pressed compacts.

From these experiments the following conclusions have been drawn: High molding pressures always give superior density and physical properties due to a more uniform and better diffused structure.

Hot-pressed compacts are found to have a very high density, and to be harder than sintered compacts of the same composition. Their microstructure reveals only little recrystallization, incomplete diffusion, and no grain growth.

The use of alloy powders leads to better properties for all sintered materials and for most of the hot-pressed compacts, and only density values and hardness figures for the highest zinc containing composition are superior in the case of compacts hot-pressed from mixed powders.

Due to the marked plasticity at elevated temperatures of commercial brass powder combinations with high zinc content, these materials appear to be particularly useful for hot molding.

METHODIC studies in recent years of a number of metals prepared by sintering compacted powders have disclosed many interesting features. In some cases basic trends in the behavior of these metals as a function of certain processing steps have been established. Such data have been (2)[1] given for sintered and hot-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. The author, Claus G. Goetzel, is assistant director of research, American Electro Metal Corp., Yonkers, N. Y. Manuscript received June 20, 1941.

pressed copper in previous publications (1), (3). Today, however, the main interest of powder metallurgists is focused on the behavior of sintered alloys rather than metals, as the practical use of pure metals is limited in industry.

Developing alloys by sintering methods is not much different from commonly known methods employed in the making of sintered pure metals. Suitable metallic powders are combined in the proper ratio by mixing and annealing treatments. The powder mixture is briquetted under pressure into a coherent mass of closely agglomerated powder particles and the compact is subjected to a heat treatment known as sintering, during which the compact remains completely or substantially in the solid state. Such heat treatment usually is conducted in a protective atmosphere, in order to prevent excessive oxidation caused by the large surface exposed in powder compacts. Details of the heat treating cycle are much dependent upon the specific material in question.

While the use of alloys with copper as a base has found a great field in the automotive industries, particularly in the case of porous bronzes, and while patent literature on this subject is voluminous, few publications give details of procedures used or of properties obtained, particularly for brass.

W. D. Jones recently investigated the performance of numerous hot-pressed copper alloys (4) using equipment described in detail in an earlier publication (5). Among numerous other copper alloys Jones studied three binary brasses with alloy powders as basic material, and four binary brasses with mixed powders as raw material.

The powdered alloys were obtained by preparing cast ingots which were pulverized afterwards to 300 mesh size. The method of pulverizing was not mentioned, but it may be assumed that a mechanical disintegrating process was used. The resulting powder particles were substantially spherical in shape. These alloy powders were molded at 5 tons per square inch at a temperature 200 degrees Cent. (390 degrees Fahr.) below the melting point of the particular composition. Hot pressing was carried out in air.

The composition of only one alloy, namely pure 70-30 brass, of minus 200 mesh size, was given together with details of procedure and results. Compacts were hot-pressed at 900 degrees Cent. (1650 degrees Fahr.) in test piece shape, and 17,000 pounds per square inch yield strength, 30,000 pounds per square inch tensile strength and 21 per cent elongation were obtained. Jones found that most

of the other compacts prepared from alloy powders, made in the above mentioned way, showed disappointingly low tensile properties.

On the other hand copper alloy compositions made by tumbling 300 mesh size powders for 8 hours showed much superior results. Such powder mixtures were first pre-pressed cold at 8 tons per square inch, and then hot-pressed in air at 4½ tons per square inch, again at temperatures approximately 200 degrees Cent. (390 degrees Fahr.) below their melting point.

Table I gives press temperatures and some physical properties for four binary brasses, as recorded by Jones.

Table I
Jones' Test Results for Hot-Pressed Binary Brass Compacts

Composition Cu-Zn	Hot Press Temperature in Degrees Cent.	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Elongation in Per Cent	Brinell Hardness
90-10	900	17,000	30,000	22	...
80-20	900	18,000	37,000	34	...
70-30	800	12,000	38,000	16	110
50-50	775	21,000	21,000	0	114

In all these specimens the microstructure was similar to that of an annealed forged alloy, but the grain size was usually very small. He concluded that in every case better results were obtainable by using the mixed powders than by employing his powdered alloys.

A very interesting investigation of diffusion between zinc and copper powders to form alpha brass alloys is reported in a paper by Owen and Pickup (6). Zinc and copper filings with particles of 70 to 140 microns in diameter were studied in various initial compositions ranging from 70 to 90 per cent copper. Powder mixtures were heated at temperatures ranging from 450 to 600 degrees Cent. (840 to 1110 degrees Fahr.) for various times up to 200 hours. The composition of the alpha phase formed was observed by precision measurement of the lattice parameter by X-ray diffraction.

In reasonable times, alloys were formed at temperatures way below the melting point of copper but only above the melting point of zinc. Diffusion was found to be more rapid with unannealed than with annealed powder, and with initially smaller than with larger particles. It was also found that for a given time of diffusion, the amount of alpha increases linearly with particle size.

On the basis of the scant literature available and of experience with pure copper, binary copper alloys were prepared from metallic

powders, and their properties investigated in a series of experiments. In this paper, results obtained with copper-zinc compacts are discussed.

Several questions of prime importance were to be studied, namely:

1. The effect of the type of raw material used on structure and properties (mixed powders compared with alloy powders).
2. The effect of the type of molding (cold pressing and sintering versus hot pressing).
3. The effect of different heat treating temperatures.
4. The effect of different molding pressures.
5. The effect of composition.
6. The degree of diffusion obtained.
7. Volumetric and weight changes of the compacts during heat treatment.

Four copper-zinc compositions of the ratios 85-15, 75-25, 65-35, and 55-45 were prepared. Test specimens were made from copper-zinc powder mixtures and from pre-alloyed brass powders. In one series of experiments compacts were cold pressed at various pressures and afterwards sintered at different temperatures; while in another series, compacts were hot-pressed into final form at different pressures and temperatures.

Raw Material

A commercial electrolytic copper powder of 100 mesh size and a purity better than 99.5 per cent was used with zinc powder of 150 mesh and a purity of better than 99.0 per cent, made by an atomizing process. The two types of powder were blended in the above-mentioned proportions in a 5-gallon tumbler for 24 hours and then reduced at 275 degrees Cent. (525 degrees Fahr.) for 2 hours in a steady stream of commercial hydrogen.

Part of the clean powder mixtures was subjected to a sinter-alloying treatment. The charges were placed in small vessels and sintered in a muffle furnace at 450 degrees Cent. (840 degrees Fahr.) for 2 hours in hydrogen. Such treatment was thought to be sufficient to promote adequate diffusion between the copper and zinc phases, particularly in view of the relatively high vapor pressure of zinc at this temperature. The heat treatment resulted in only a

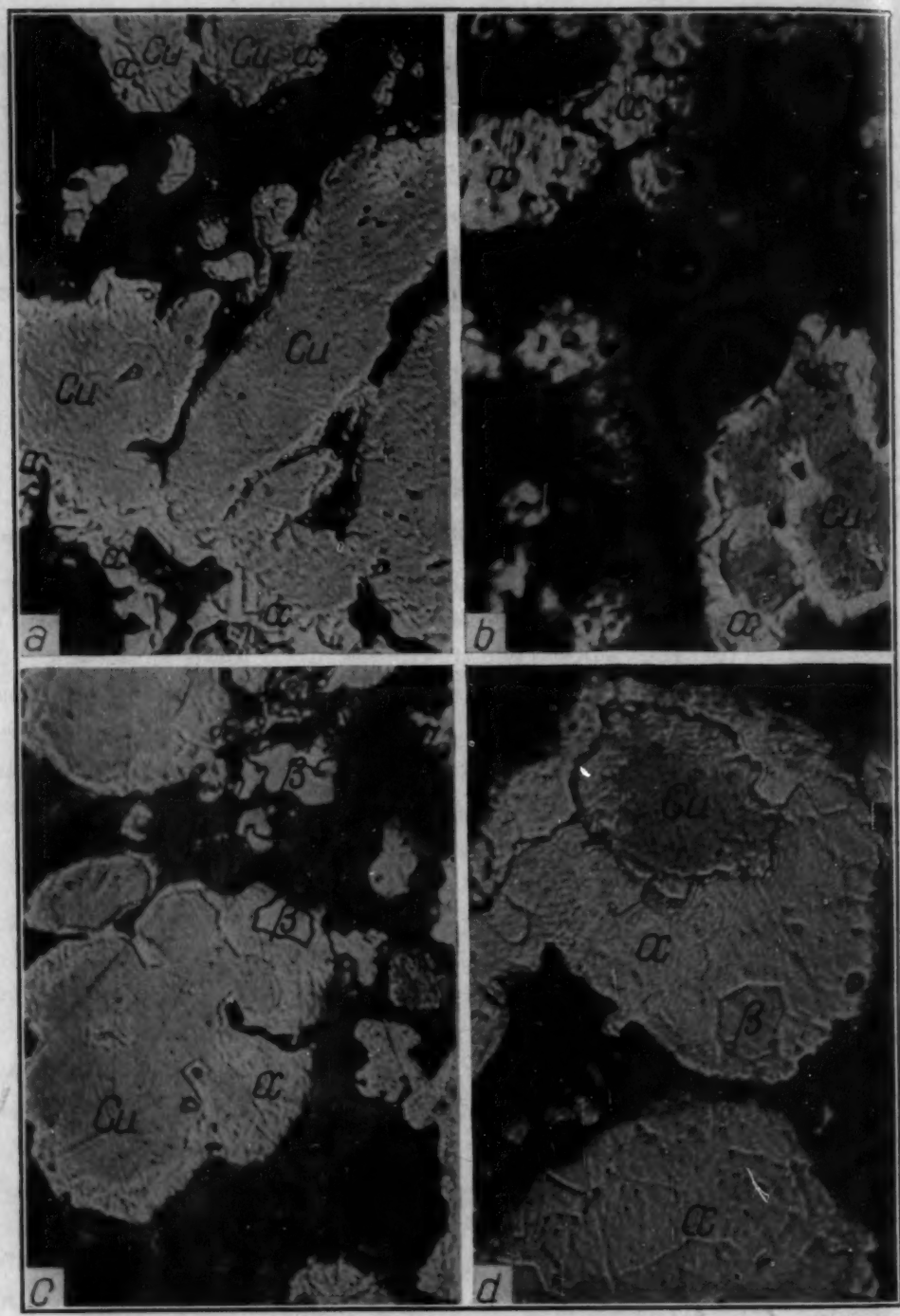


Fig. 1—Microstructure of Brass Powders, Made by Sintering at 450 Degrees Cent. × 1000. (Etched With 50 Per Cent Solution of HNO_3 in Alcohol).

a. 85-15 Copper-Zinc Composition; b. 75-25 Copper-Zinc Composition; c. 65-35 Copper-Zinc Composition; d. 55-45 Copper-Zinc Composition.

slight sintering of the powder mass, which could be pulverized by mechanical means without difficulties. While the general appearance

of the pre-alloyed powder combinations was satisfactory from a standpoint of uniformity of the product, microscopic examination disclosed that diffusion in many instances was only partially completed.

The photomicrographs of Fig. 1 represent the structure of powder particles of the four different combinations after the pre-alloying treatment. In the case of the 85-15 composition (Fig. 1a), many particles still consist of pure copper with only border zones of alpha Cu-Zn solid solution, while for the 75-25 combination (Fig. 1b) the diffusion of zinc into copper was considerably deeper, the smaller particles and most of the larger particles being completely converted into alpha-brass. The 65-35 alloy powder (Fig. 1c) consisted of three constituents, pure copper, alpha and beta brass, of which alpha-brass was most abundant. In the case of 55-45 Cu-Zn the alpha constituent again appears predominant, with beta as a minor constituent, and pure copper-rich pink patches occasionally detectable (Fig. 1d). The zones of transition of copper to alpha or alpha to beta are sometimes progressive, displaying a gradual change in color over a narrow zone, but in most particles a sharp demarcation line between the constituents is recognizable.

Processing and Testing

Pressing and heat treating methods for the different powder combinations were substantially the same as reported in detail elsewhere (3). A cold molding pressure of 2 tons per square inch prior to hot pressing was found to be insufficient for the pre-alloyed powders on account of increased resistance of the powder to plastic flow under pressure and had to be raised to 5 tons per square inch.

The special equipment available for hot pressing permitted the production of only small cylindrical compacts, 5/8 inch in diameter and 1/2 to 5/8 inch high. For this reason testing of physical properties was limited to density, hardness and compressive properties together with a close examination of the microstructure of the various products obtained. In addition, volumetric and weight changes resulting from sintering were investigated.

Test Results

Volume and Weight Changes—During sintering, compacts of

all four combinations underwent considerable changes in volume, in some cases approaching as much as 50 per cent expansion. Changes in weight were less marked. The actual values are plotted versus compacting pressure in Figs. 2 and 3. Both volume and weight changes are the results of complex effects of various factors. In the case of volume changes they are:

(a) Release of stresses originating from the cold pressing operation.

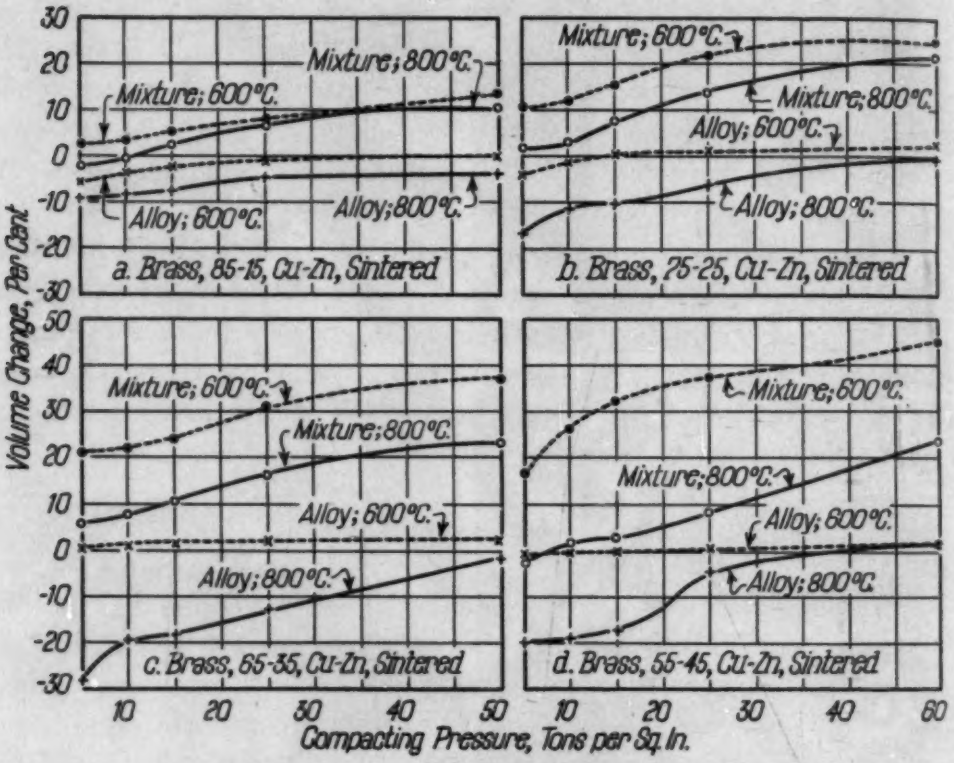


Fig. 2—Volume Change Versus Compacting Pressure.

(b) Gas adsorption and entrapping of air at room temperature and gas evolution at elevated temperatures.

(c) Shrinkage, caused by sintering, diffusion, grain growth, gravity forces, creep phenomena, etc.

As seen in Fig. 2 expansion in volume progresses with increase in the initial pressure and with increase in zinc content, while an increase in sintering temperature shows trends towards shrinkage as known in the case of copper (1), (2). The volume increase with rising zinc content may be explained by the fact that the powdered zinc constituent of the compacts, having a large surface, gives off a large amount of zinc vapor at the sintering temperature. An addi-

tional factor is the evolution of gases such as oxygen which would combine with hydrogen to form water vapor. In support of this assumption is the fact that volume changes during sintering of pre-alloyed compacts of all compositions are considerably shifted to the negative side in the diagrams. In this case little or no free zinc is left in the compacts which could give off vapor or adsorbed gases.

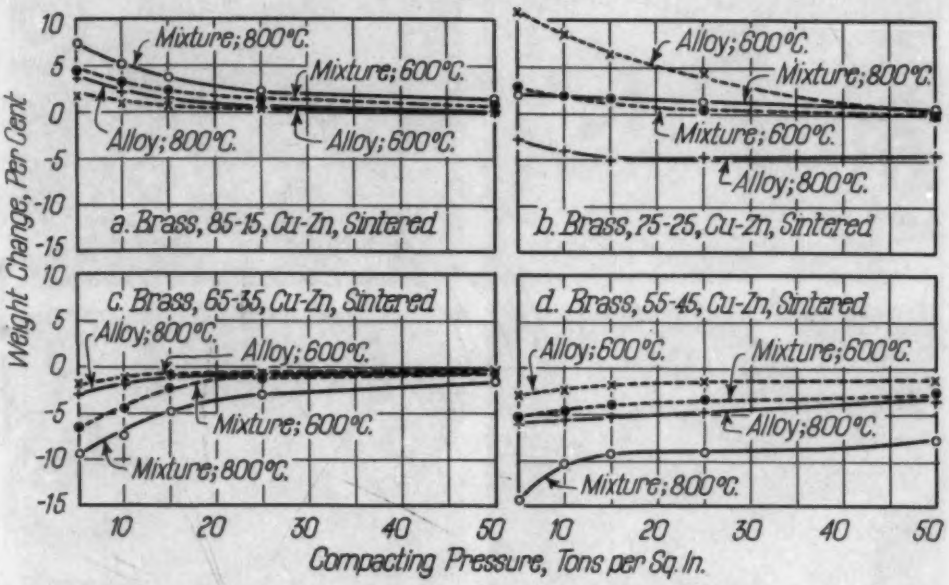


Fig. 3—Weight Change Versus Compacting Pressure.

In the case of weight changes during sintering the factors contributing to such changes are:

(a) Oxidation of zinc in the heat treating atmosphere.
(b) Adsorption of gases such as hydrogen.
(c) Zinc losses by evaporation.

As the diagrams of Fig. 3 show, positive weight changes were encountered only at the lower zinc contents and at low compacting pressures. This indicates that weight increases due to gas adsorption or oxidation are negligible in comparison to the losses caused by zinc evaporation. This loss in weight is particularly evident for the high zinc combinations. For the 65-35 and 55-45 compositions weight losses are more marked for powder mixture compacts as compared with alloy powder compacts and in both cases the higher sintering temperature caused greater losses.

Microstructure—The structures of sintered and hot-pressed 85-15 Cu-Zn compacts are shown in the photomicrographs of Figs. 4 and 5.

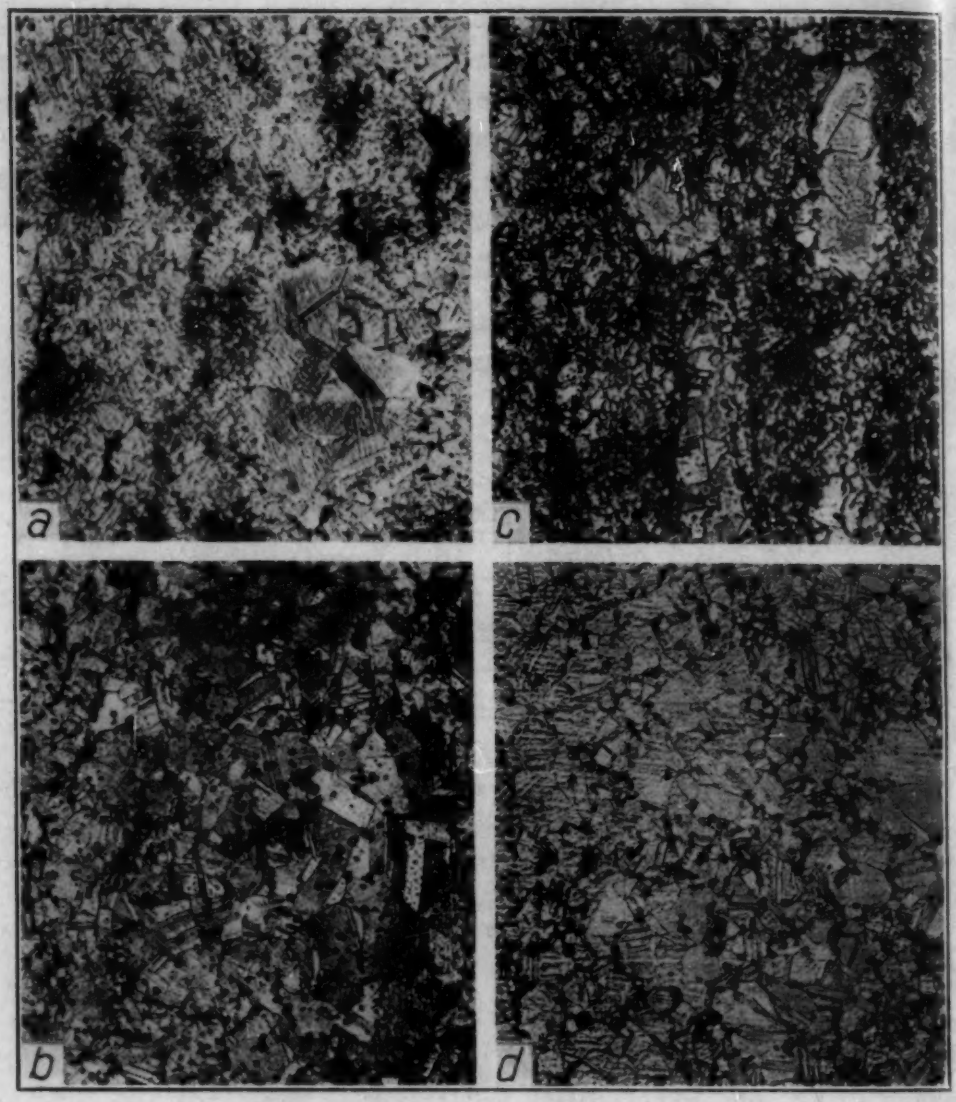


Fig. 4—Microstructure of Sintered 85-15 Brass Compacts. × 200.

a. Compact pressed at 50 tons per square inch from mixed powders and sintered at 600 degrees Cent. for 1 hour (etched with 1:1 NH_4OH plus 10 per cent ammonium persulphate solution).

b. Compact pressed at 50 tons per square inch from mixed powders and sintered at 800 degrees Cent. for 1 hour (etched with 50 per cent HNO_3 in alcohol).

c. Compact pressed at 50 tons per square inch from pre-alloyed powder and sintered at 600 degrees Cent. for 1 hour (etched with 50 per cent HNO_3 in alcohol).

d. Compact pressed at 50 tons per square inch from pre-alloyed powder and sintered at 800 degrees Cent. for 1 hour (etched with 50 per cent HNO_3 in alcohol).

After sintering at 600 degrees Cent. (1110 degrees Fahr.) for 1 hour the structure of the powder mixture compact remains obscure and nonhomogeneous (Fig. 4a). Boundary areas of original particles of copper are still visible, and diffusion and formation of alpha-brass has taken place in only some areas. In addition a great number

of cavities and occasional large holes help to distort the picture. After sintering the same material at 800 degrees Cent. (1470 degrees Fahr.) for 1 hour, the structure appears to be much more uniform (Fig. 4b). Alpha solid solution of fine grain size is predominant, and only occasionally copper-rich areas (appearing pink under the microscope) or zinc-rich inclusions (appearing grayish) remain visible. Porosity is similar in character to the specimen shown in Fig. 4a.

Pre-alloyed compacts after sintering at 600 degrees Cent. (1110 degrees Fahr.) still show a nonhomogeneous structure with most of the large particles disclosing marked diffusion zones with copper-rich areas in the center and alpha-brass at the periphery (Fig. 4c). On the other hand most of the small particles have been completely transformed into alpha-brass. The structure remains somewhat obscured by pores and occasional zinc-rich inclusions.

Sintering of pre-alloyed compacts at 800 degrees Cent. (1470 degrees Fahr.) for 1 hour yields a more homogeneous structure of fine-grained alpha-brass (Fig. 4d). Copper-rich or zinc-rich areas are hardly detectable, and with the exception of the presence of numerous pores, the material appears to be uniform.

Quite a different picture is observed in the case of hot-pressed compacts. Fig. 5a represents the structure of a powder mixture compact after hot pressing under hydrogen at 300 degrees Cent. (570 degrees Fahr.) at 50 tons per square inch. Little alloying has taken place between the copper and the zinc during this treatment. Only occasional areas of alpha solid solution can be detected, while the bulk of the material consists of copper particles (of pink color, appearing light in Fig. 5a) and zinc particles or zinc-rich phases (etching and appearing black). Some of the larger copper particles showed signs of recrystallization. Only some of the grayish zinc particles showed microscopic pores in their center after polishing, while in general the material appeared to be dense.

The same material hot-pressed at 500 degrees Cent. (930 degrees Fahr.) shows advanced diffusion of the zinc and copper. Alpha-brass (appearing yellow) is formed throughout the field, particularly in the smaller particles. Large copper-rich particles and some zinc-rich areas are still visible, and initial particle boundaries have not yet disappeared, although everywhere recrystallization has commenced. The material pressed at 50 tons per square inch is practically free from porosity (Fig. 5b).

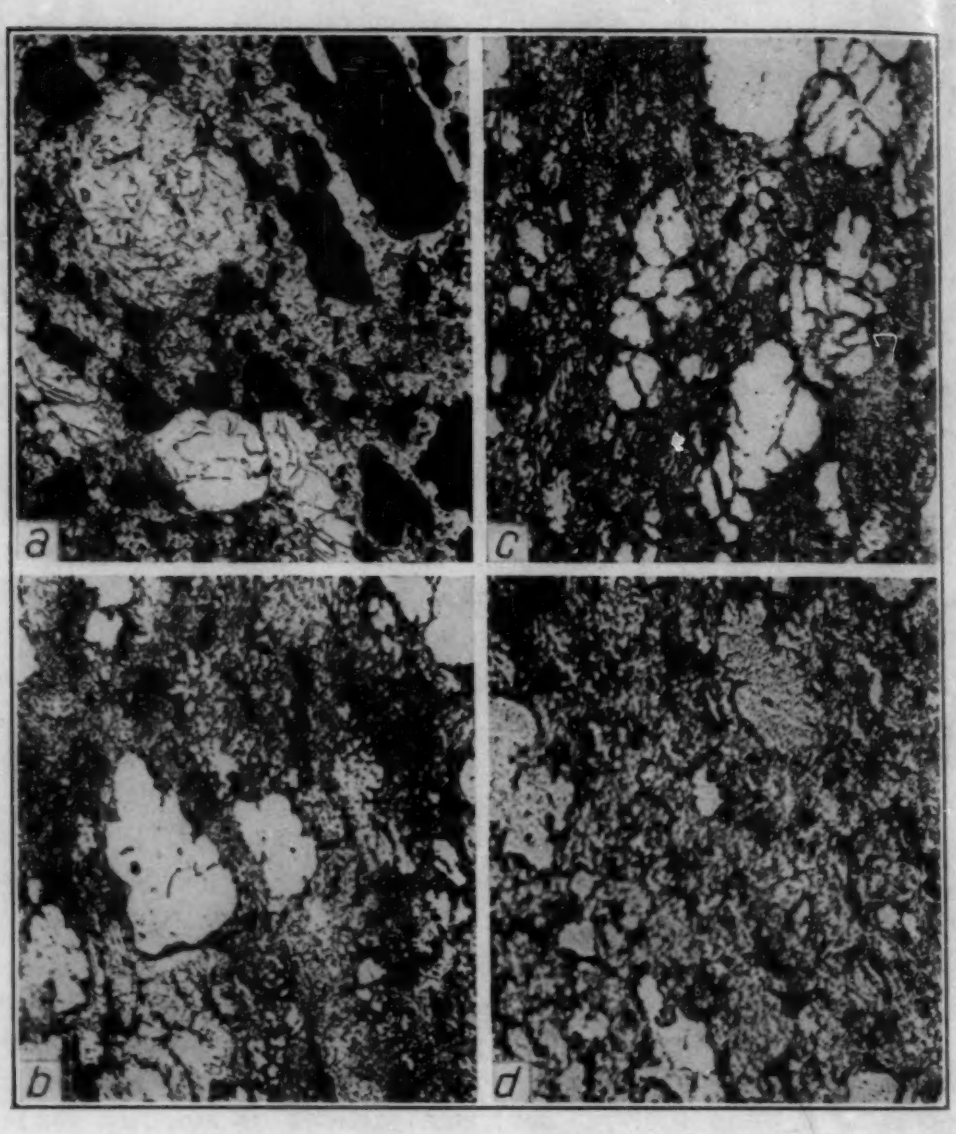


Fig. 5—Microstructure of Hot-Pressed 85-15 Brass Compacts. × 200.

a. Compact pressed from mixed powders at 50 tons per square inch at 300 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

b. Compact pressed from mixed powders at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

c. Compact pressed from pre-alloyed powder at 50 tons per square inch at 300 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

d. Compact pressed from pre-alloyed powder at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

The structure of pre-alloyed compacts, hot-pressed at 300 degrees Cent. (570 degrees Fahr.) (Fig. 5c), is somewhat similar in appearance to the mixed powder group identically treated. Alpha solid solution areas can be seen throughout the compacts, but many larger particles still show copper-rich cores. Also, occasional zinc-

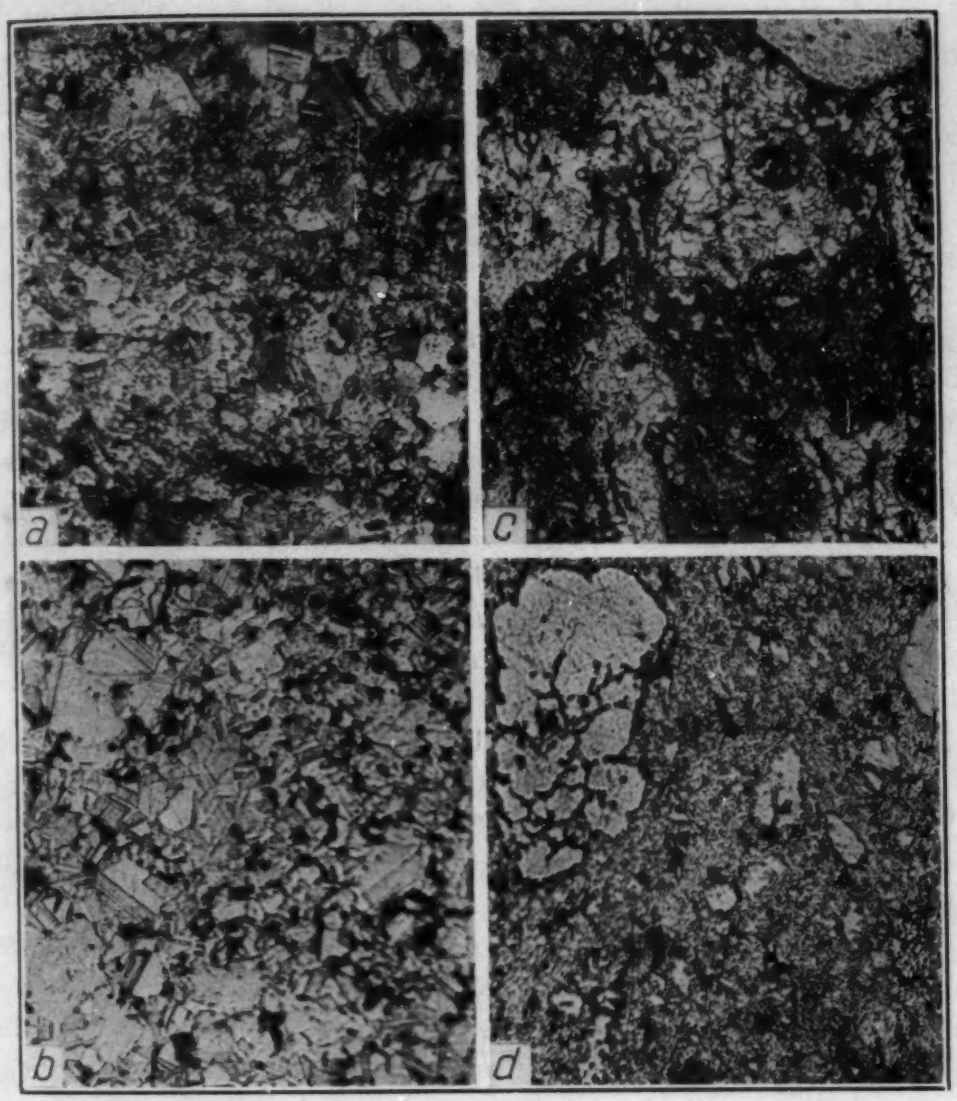


Fig. 6—Microstructure of Sintered and Hot-Pressed 75-25 Brass Compacts. × 200.

a. Compact pressed from mixed powders at 50 tons per square inch and sintered at 800 degrees Cent. for 1 hour (etched with 50 per cent solution of HNO_3 in alcohol).

b. Compact pressed from pre-alloyed powder at 50 tons per square inch and sintered at 800 degrees Cent. for 1 hour (etched with 50 per cent HNO_3 in alcohol).

c. Compact hot-pressed from mixed powders at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

d. Compact hot-pressed from pre-alloyed powder at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

rich particles can be found. Recrystallization is less evident that in the previous case on account of the lower press temperature. In the case of compacts pressed at 50 tons per square inch the structure shows only occasional small cavities.

The particles remain outlined also for the pre-alloyed compacts

hot-pressed at 500 degrees Cent. (930 degrees Fahr.). Recrystallization within many particles is detectable. Again, in the case of 50 tons per square inch pressures, the material appears quite dense (Fig. 5d). The structure consists of a predominant alpha phase of uniform golden color within the great majority of particles. Only occasionally particles with copper-rich cores or zinc-rich inclusions can be detected.

The structures of compacts of the 75-25 composition, both sintered and hot-pressed (Fig. 6), resemble those described in detail for the 85-15 composition. In the compacts prepared from the powder mixture the structure is still very nonhomogeneous with some copper-rich areas, particularly in the central regions of the original particles, and with alpha-brass of varying composition in other areas. In the case of the pre-alloyed sinter metal the structure is more uniform, with only occasional signs of concentration gradients. The original particles have been completely replaced by a polygonal crystal structure after sintering at 800 degrees Cent. (1470 degrees Fahr.).

In the specimens hot-pressed from the powder mixture, little diffusion has taken place during the short time the specimens were subjected to heat and, consequently, the structure remains nonuniform, very similar to the 85-15 composition. In compacts pressed at 500 degrees Cent. (930 degrees Fahr.) no zinc or zinc-rich phases could be detected. Evidently the liquid zinc at such temperature has completely alloyed with the copper. In the case of pre-alloyed powder, the structure appears very uniform in composition with little evidence of incomplete diffusion, although the original particle pattern has not yet given way to a polygonal grain structure.

Fig. 7 represents the microstructure of sintered and hot-pressed brass of the 65-35 composition. For sintered compacts there is little difference noticeable if the structure of pre-alloyed compacts (Fig. 7b) is compared with that of specimens prepared from the powder mixture (Fig. 7a). In both cases alpha-brass is predominant and is present as polygonal grains of medium size. The structure is somewhat obscured by the presence of numerous pores and occasional inclusions of zinc-rich phases. However, the previously noted advantage of pre-alloyed compacts of showing a more diffused and uniform grain structure has almost completely vanished in the case of compacts sintered at 800 degrees Cent. (1470 degrees Fahr.).

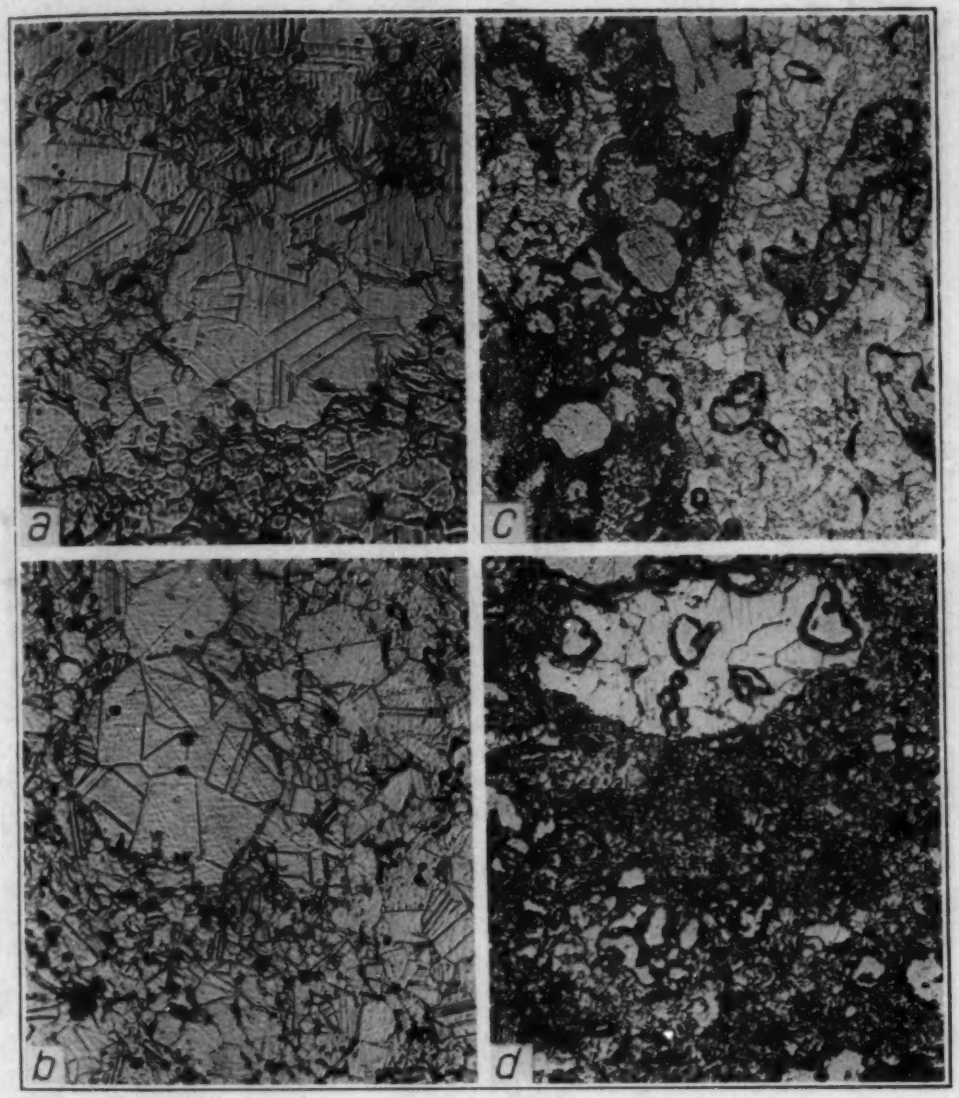


Fig. 7—Microstructure of Sintered and Hot-Pressed 65-35 Brass Compacts. × 200.

a. Compact pressed from mixed powders at 50 tons per square inch and sintered at 800 degrees Cent. for 1 hour (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

b. Compact pressed from pre-alloyed powder at 50 tons per square inch and sintered at 800 degrees Cent. for 1 hour (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

c. Compact hot-pressed from mixed powders at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

d. Compact hot-pressed from pre-alloyed powder at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

This may be explained by the proximity of this sintering temperature to the melting temperature range.

As in the previous cases, the structure of hot-pressed specimens is much more dense and compact. Diffusion is not complete, particularly in the case of the compacts prepared from the powder mix-

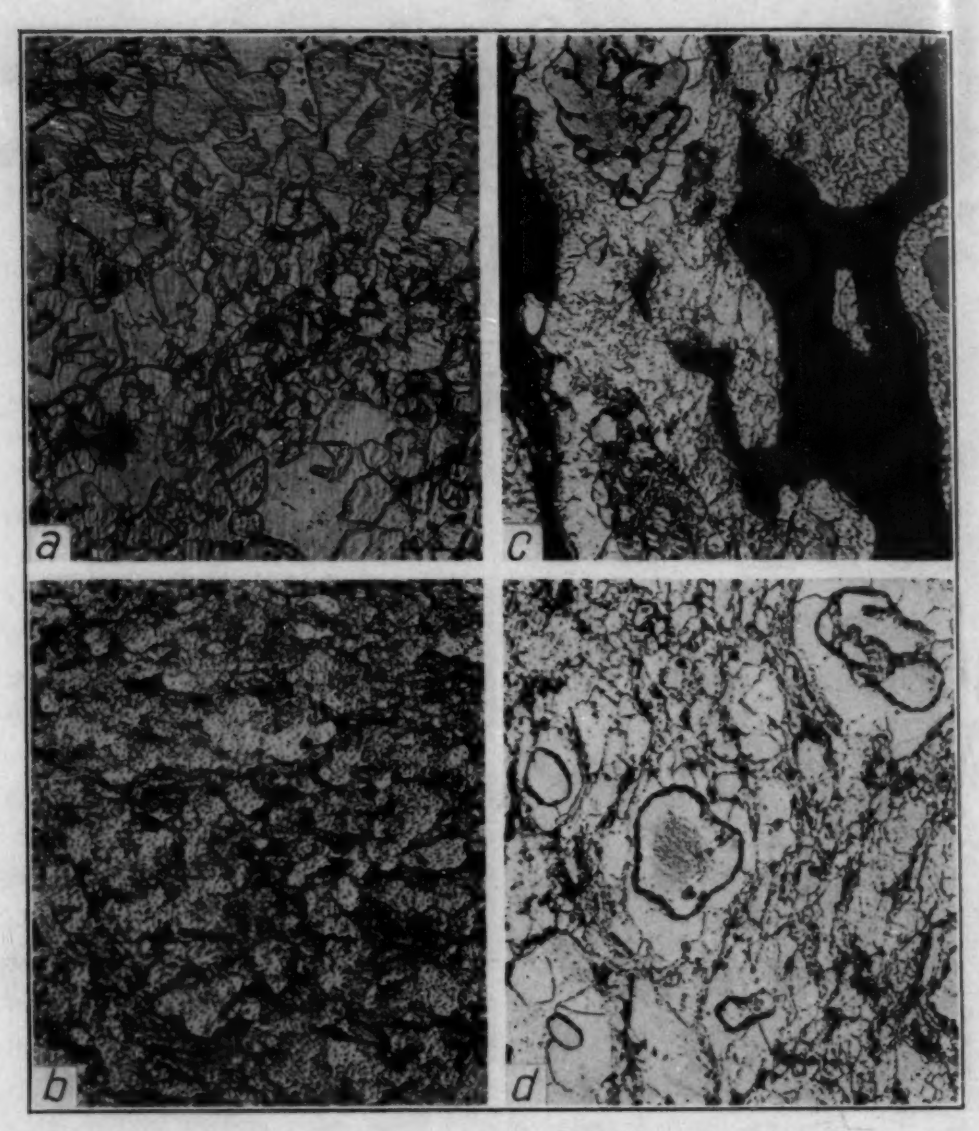


Fig. 8—Microstructure of Sintered and Hot-Pressed 55-45 Brass Compacts. × 200.

a. Compact pressed from mixed powders at 50 tons per square inch and sintered at 800 degrees Cent. for 1 hour (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

b. Compact pressed from pre-alloyed powder at 50 tons per square inch and sintered at 800 degrees Cent. for 1 hour (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

c. Compact hot-pressed from mixed powders at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

d. Compact hot-pressed from pre-alloyed powder at 50 tons per square inch at 500 degrees Cent. (etched with 1:1:1 NH_4OH, H_2O_2, H_2O).

tures. Besides alpha-brass, which is predominant, occasional isolated zinc or zinc-rich areas as well as copper-rich areas in the center of large particles are recognizable. Only few isolated spots of beta-brass are visible.

The microstructure of sintered and hot-pressed material of the

55-45 Cu-Zn composition is shown in Fig. 8. In the case of the sintered compacts the structure consists of an intimate mixture of alpha and beta brass after heat treatment at 800 degrees Cent. (1470 degrees Fahr.), regardless of the type of initial powder used. Compacts prepared from the pre-alloyed powder appear to be slightly

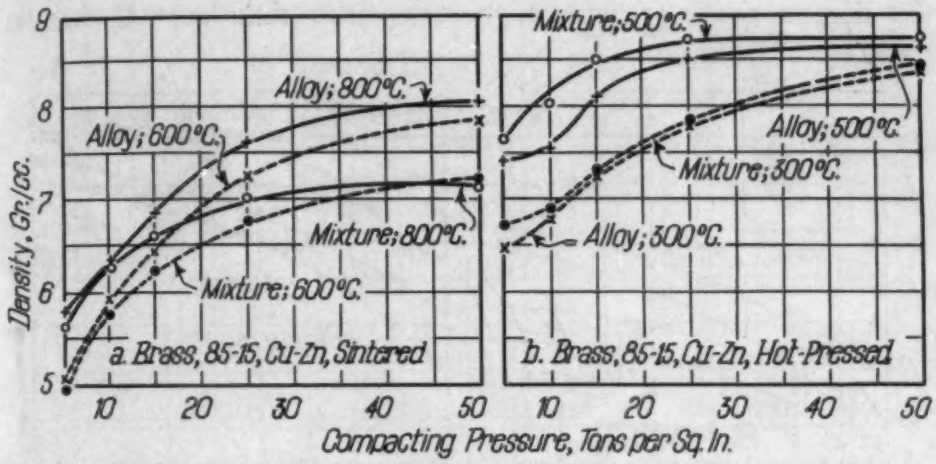


Fig. 9—Density Versus Compacting Pressure for 85-15 Copper-Zinc Compacts.

more uniform in the distribution of the two constituents, and showed no copper-rich or zinc-rich areas. Also such material appears to have slightly less porosity than the specimens prepared from the powder mixture, although it is excessive in both cases.

Quite different is the picture for the hot-pressed material. In the case of compacts hot-pressed at 500 degrees Cent. (930 degrees Fahr.), the material appears dense, and the crystallization of the structure more advanced than in the other compositions probably due to the large amount of zinc present in the liquid state at the temperature of pressing. However, the structure for compacts of both types of powder lacks homogeneity. In the case of compacts prepared from the powder mixture the structure shows a continuous network of zinc-rich constituents (etching black) which completely envelops a matrix of alpha-brass plus occasional particles of undiffused copper (Fig. 8c). In the pre-alloyed compacts grain clusters of alpha and beta solid solution are only occasionally interrupted by partly dissolved particles with copper-rich cores (Fig. 8d).

Density—Density determinations were carried out employing the weight-volume method for all specimens. Dense specimens were weighed in air and water and the results computed for check pur-

poses. Both methods were found to be in agreement within 1 per cent.

Fig. 9 shows diagrams in which density is plotted against compacting pressure. All four curves in diagram 9a, referring to sintered compacts, have hyperbolic shapes and positive slopes, a characteristic already noted on pure copper (3). Treatment at 800 degrees Cent. (1470 degrees Fahr.) yields higher densities than at 600 degrees

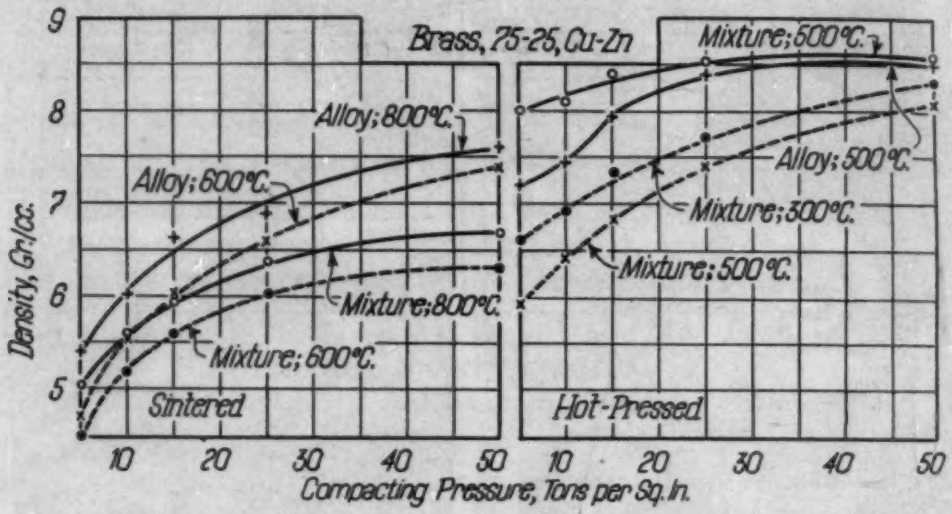


Fig. 10—Density Versus Compacting Pressure for 75-25 Copper-Zinc Compacts.

Cent. (1110 degrees Fahr.), and pre-alloyed powder compacts show superior data in comparison with compacts prepared from the mixture. These results are in agreement with observations made during the determination of weight and volume changes during sintering (Figs. 2a and 3a). Density values in general are low; even compacts sintered close to the melting point do not exceed 90 per cent of the ideal density.

Diagram 9b represents a similar graph for hot-pressed compacts. The general character of the curves is the same as in the case of the sintered specimens. Density rises with increasing molding pressure in concave-upwards shaped curves of positive slopes. The specimens treated at the higher temperature show superior results as in the case of the sintered compacts. However, in the case of hot-pressed material, compacts prepared from the powder mixture give greater densities than those pressed from the pre-alloyed powder. This may be attributed to an impaired plasticity of the pre-alloyed powders, which offer more resistance to deformation under heat and pressure

than mixtures of powders, of which the main constituent, copper, is of great deformability. The powder mixture compacts pressed at 500 degrees Cent. (930 degrees Fahr.) and high pressures yield densities either approaching or reaching the ideal density for 85-15

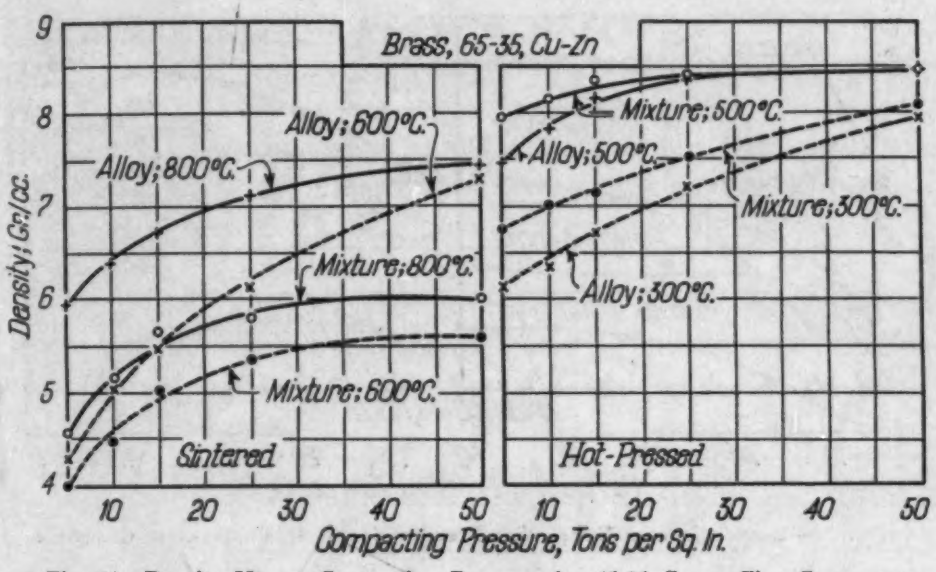


Fig. 11—Density Versus Compacting Pressure for 65-35 Copper-Zinc Compacts.

brass (8.75 grams per cubic centimeter). Results for the 75-25 combinations are plotted in Fig. 10.

The character of all curves shown in the diagrams for sintered and hot-pressed compacts is the same as in the case of the 85-15 composition, and actual values are in close proximity. High temperature treatment in both cases yields superior densities and sintered material again is inferior to hot-pressed compacts. While the prealloyed powder yields higher densities for sintered material, the reverse holds for hot-pressed compacts. Peak values of 8.6 grams per cubic centimeter at pressures above 25 tons per square inch at 500 degrees Cent. (930 degrees Fahr.) press temperature are obtained with mixed powder compacts.

For the 65-35 composition (Fig. 11) the character of the curves is the same and hot-pressed material again shows great superiority in density over sintered metal. Alloy powder compacts after sintering yield higher values than compacts prepared from the mixture, and an increase in sintering temperature from 600 to 800 degrees Cent. (1110 to 1470 degrees Fahr.) causes considerable improvement in density, particularly for the higher compacting pressures.

In the case of hot-pressed material, compacts pressed at 500 degrees Cent. (930 degrees Fahr.) are far superior to those pressed at 300 degrees Cent. (570 degrees Fahr.), and reach a density close to 8.5 grams per cubic centimeter at pressures above 25 tons per

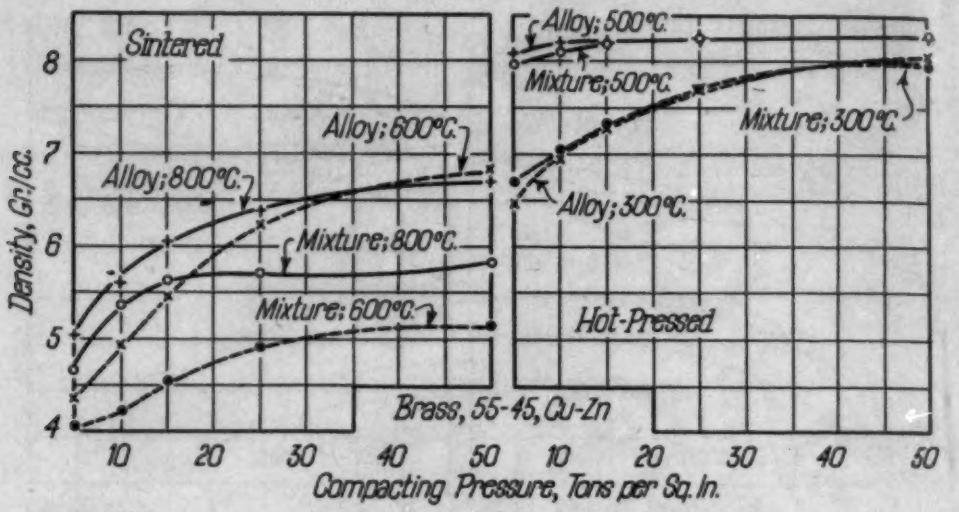


Fig. 12—Density Versus Compacting Pressure for 55-45 Copper-Zinc Compacts.

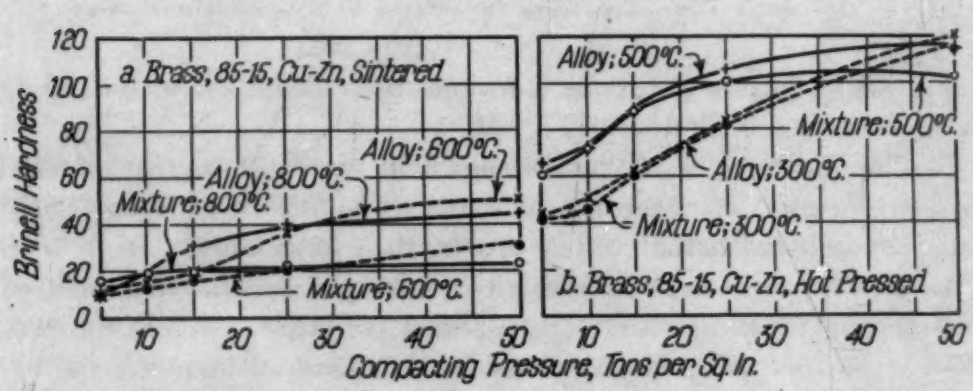


Fig. 13—Brinell Hardness Versus Compacting Pressure for 85-15 Copper-Zinc Compacts.

square inch. As previously observed, compacts prepared from the mixture prior to hot pressing are slightly denser than compacts pressed from the pre-alloyed powder.

For the 55-45 Cu-Zn composition, the tendency of the density data to rise with increasing molding pressure in a hyperbolic fashion is again recognizable (Fig. 12). Also, as in the previous cases, density data of the hot-pressed compacts are far superior to those for sintered compacts. Due to the high zinc content, the curves are generally lower than in previous cases. However, values of 8.25

grams per cubic centimeter as obtained with compacts hot-pressed at 500 degrees Cent. may be considered close to normal density of such material. The density maximum is already obtained at fairly low pressures of 10 to 15 tons per square inch and maintained at its peak thereafter. This is rather remarkable and is a clear indication of the great plasticity of the material at the temperature of pressing.

The arrangement of the curves in the diagrams is less orderly than in the previous cases, but the superiority in density of the sintered alloy powder versus mixed powder compacts is again noticeable. Also, as in the case of the other compositions, compacts sintered or hot-pressed at the higher temperatures in most cases show higher values.

Hardness—Hardness tests were made on the same specimens, using a Rockwell tester and the "E" scale. The original values were converted into Brinell units. For the 85-15 composition they are

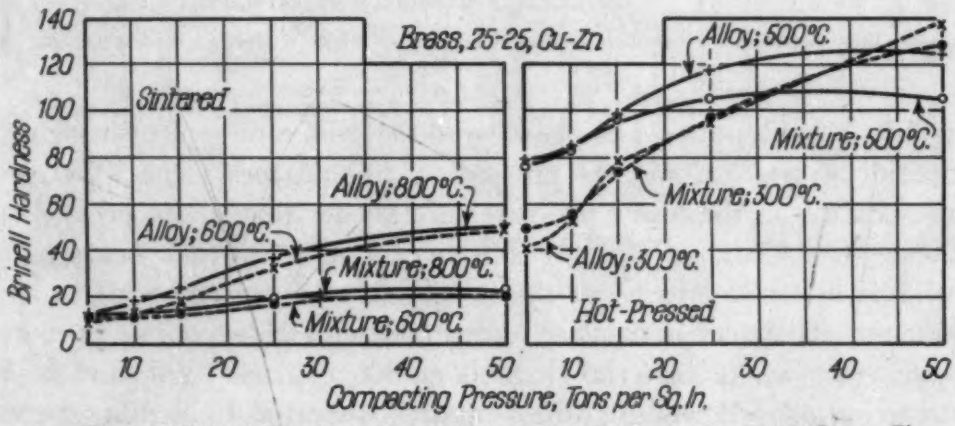


Fig. 14—Brinell Hardness Versus Compacting Pressure for 75-25 Copper-Zinc Compacts.

shown in Fig. 13, where they are plotted versus molding pressures for sintered and hot-pressed material.

Although in Fig. 13a frequent crossings of the curves somewhat distort the picture, the superiority of the pre-alloyed compacts is apparent. Also, for the higher initial pressures the specimens sintered at the lower temperature are harder, due to residual strains caused by the cold pressing operation. Although hardness rises with increasing initial pressures, the values of these sintered 85-15 brass compacts in no case surpass 50 Brinell units. The low hardness may chiefly be attributed to the presence of excessive porosity in most of these specimens.

The situation in the case of hot-pressed material is quite different as is illustrated in Fig. 13b. While the tendency of the curves to rise in a hyperbolic fashion with increasing molding pressure is again noticeable, hardness data reach much higher figures, approach-

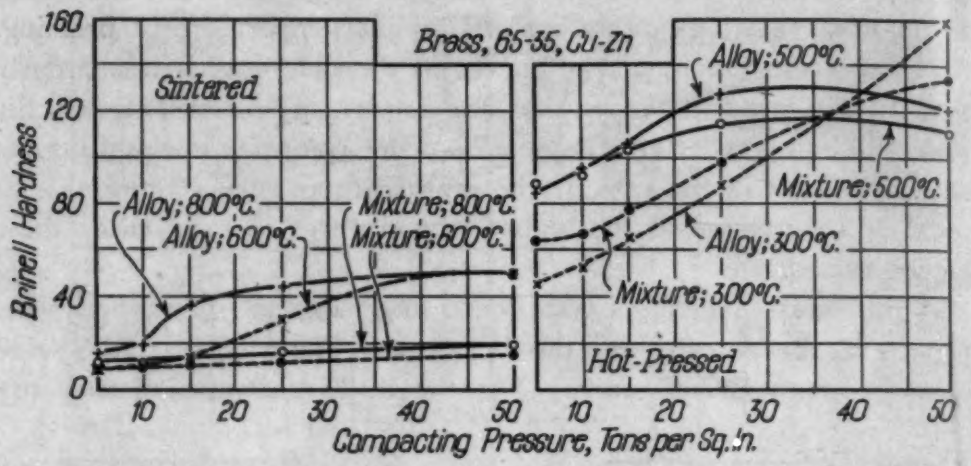


Fig. 15—Brinell Hardness Versus Compacting Pressure for 65-35 Copper-Zinc Compacts.

ing 120 Brinell units. The pre-alloyed material always shows slightly superior values. Compacts pressed at 500 degrees Cent. (930 degrees Fahr.) at the lower pressures are harder than those pressed at 300 degrees Cent. (570 degrees Fahr.), but at 50 tons per square inch the material pressed at the lower temperature has a slight advantage. This fact is in close agreement with observations on pure copper (3) where material pressed at 300 degrees Cent. and high pressures also showed hardness figures superior to similar metal pressed at higher temperatures, and where this phenomenon was explained by the beginning of recovery of the metal at temperatures in excess of 300 degrees Cent.

Hardness values for the 75-25 composition are plotted versus molding pressure in Fig. 14. The general character of the curves in these diagrams remains the same as in the case of the 85-15 combination. In the case of sintered metal, the higher heat treating temperature causes a slight improvement in the hardness over the lower sintering temperature.

The same is true for the hot-pressed material, but only at the low-molding pressures. At pressures above approximately 30 tons per square inch, hardness of compacts pressed at 300 degrees Cent. becomes higher than that of similar compacts, pressed at 500 degrees

Cent. This was also experienced with material of the 85-15 composition where an explanation has been given. Peak hardness values of 135 Brinell units were reached, surpassing maximum values of the 85-15 composition.

Hardness test results, for the 65-35 composition, as plotted in the diagrams of Fig. 15, resemble those of the previous compositions. The general trend remains the same, and the figures rise with increasing molding pressure. As in the previous cases, hot-pressed compacts are much harder than sintered metal, and in certain cases

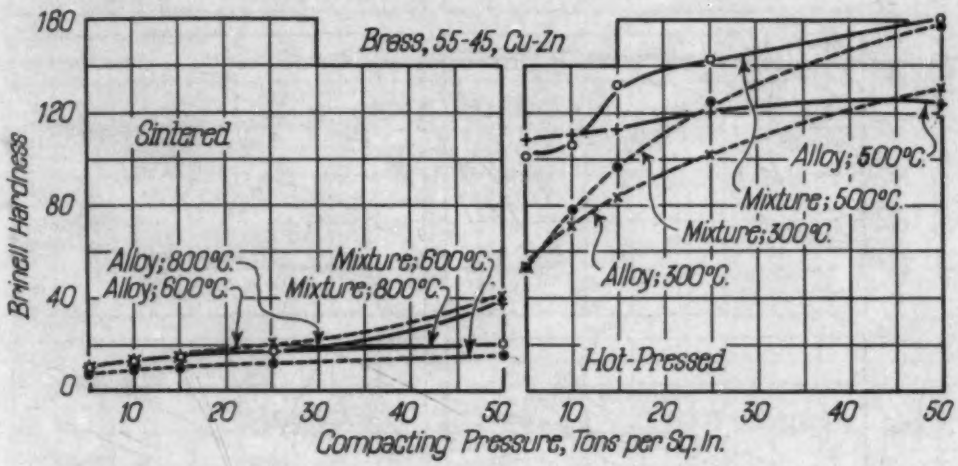


Fig. 16—Brinell Hardness Versus Compacting Pressure for 55-45 Copper-Zinc Compacts.

hardness reaches 150 Brinell units. Compacts made from alloy powders are harder than those made from powder mixtures, both for sintered and hot-pressed material. The high temperature treatment yields superior results in the case of sintered compacts and the case of hot-pressed compacts below approximately 30 tons per square inch molding pressure. Above this pressure the material pressed at the lower temperature is harder.

The previously experienced tendency for hardness to rise with increasing molding pressure is also seen in the case of the 55-45 composition (Fig. 16). For the sintered material (Fig 16a), the actual values are lower than in the case of the 65-35 composition (Fig. 15a). However, the opposite is the case for hot-pressed compacts, particularly at lower molding pressures. A superiority in hardness for hot-pressed compacts prepared from the powder mixtures, resulting in peak values of 160 Brinell units, is peculiar and in contrast to the other compositions. It may be explained by

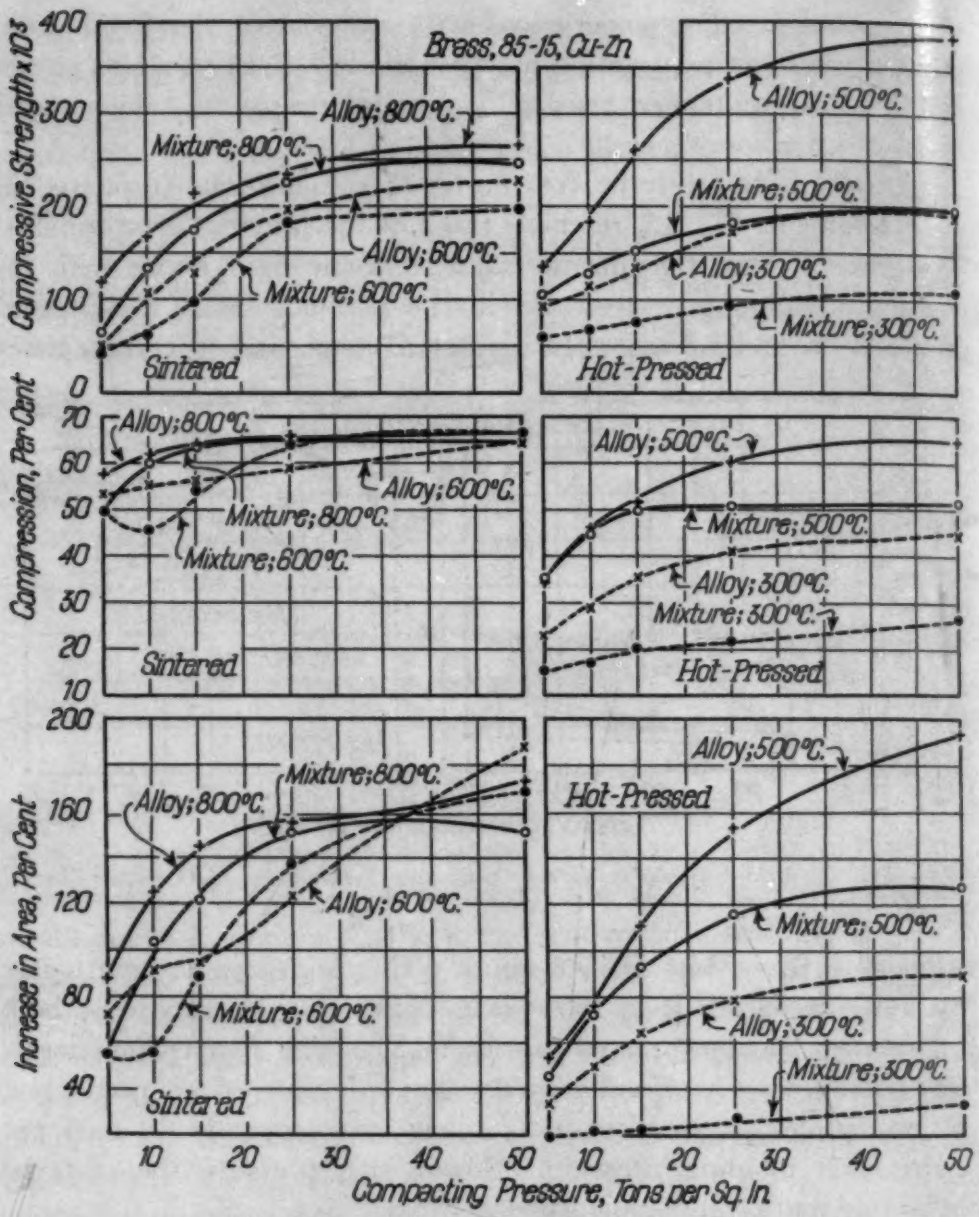


Fig. 17—Compressive Properties Versus Compacting Pressure for 85-15 Copper-Zinc Compacts.

the presence of the network of zinc-rich constituents which no doubt display great hardness and brittleness.

Compressive Properties—Compression tests were made in a similar manner as in the investigation on pure copper (3).

The results of tests on the 85-15 composition are given in Fig. 17; the left section showing compressive strength, compression and increase in area versus initial pressure for sintered compacts, and

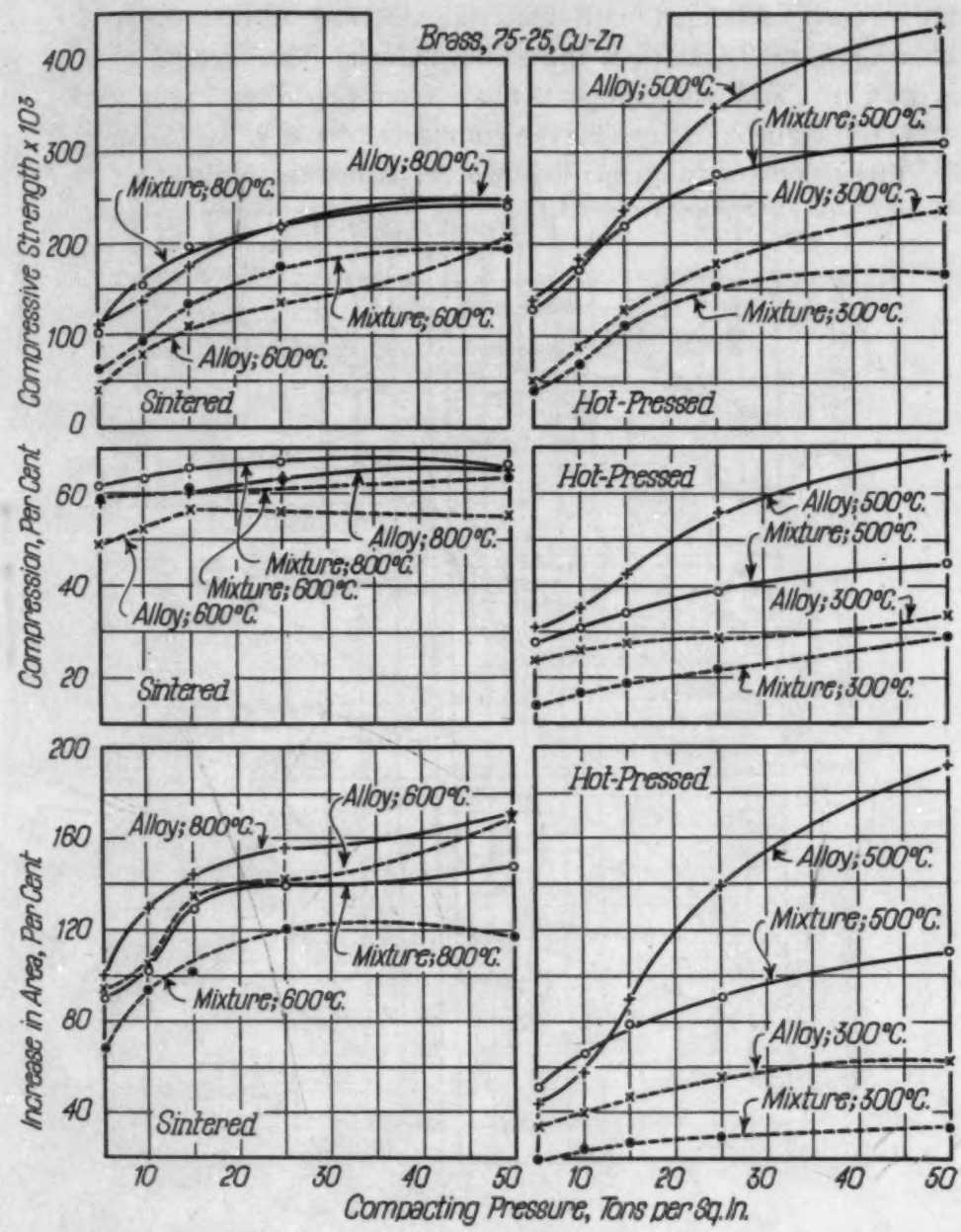


Fig. 18—Compressive Properties Versus Compacting Pressure for 75-25 Copper-Zinc Compacts.

the right section showing similar data for hot-pressed material.

Again, all curves show the distinct tendency of a positive slope with rising pressure. In most cases they display a hyperbolic character with a concave-upwards course.

In Fig. 17a the compressive strength curves for compacts sintered at 600 and 800 degrees Cent. (1110 and 1470 degrees Fahr.)

are orderly arranged with material sintered at 800 degrees Cent. showing better data than the same material heat treated at 600 degrees Cent., and with compacts made from pre-alloyed powder always showing slight superiority over compacts prepared from the powder mixture. This arrangement, however, is not maintained in the case

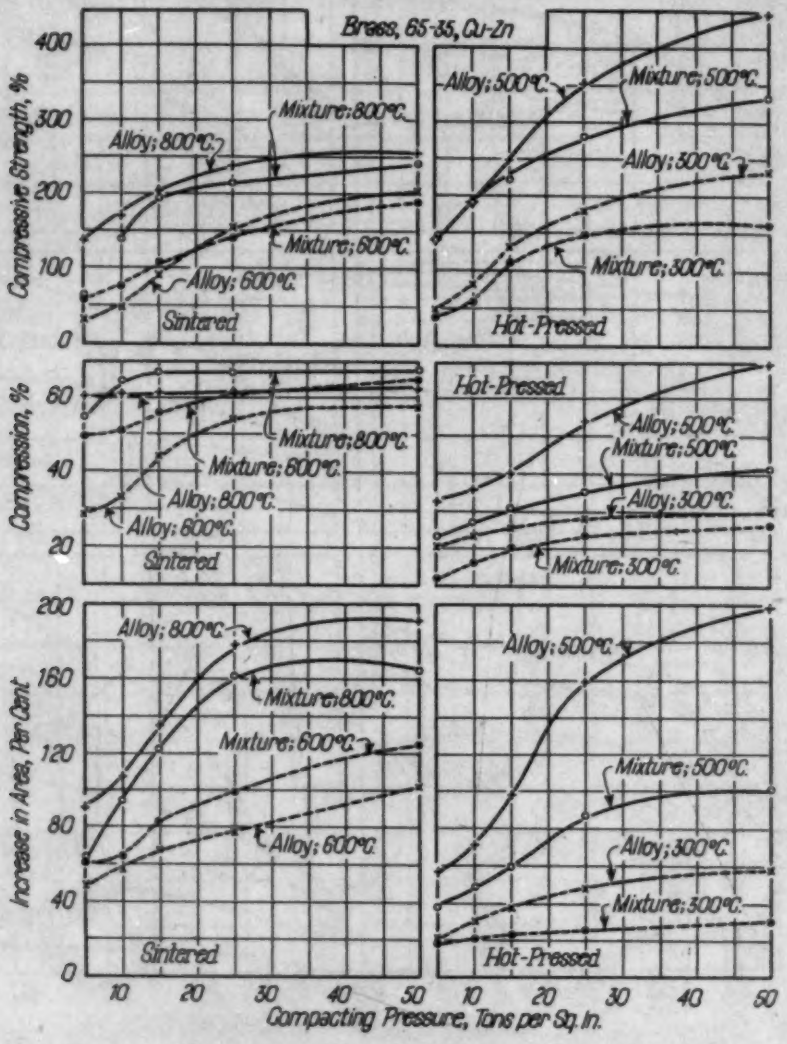


Fig. 19—Compressive Properties Versus Compacting Pressure for 65-35 Copper-Zinc Compacts.

of compression and increase in area, where frequent crossings complicate the picture. However, the general rule is that the material sintered at the higher temperature shows more deformability (compression and increase in area prior to fracturing).

As shown in Fig. 17b the values obtained with hot-pressed material are spread more over the diagrams. The curves for hot-pressed material are orderly arranged in all three diagrams.

The great superiority in compressive strength of the material developed from the pre-alloyed powder and hot-pressed at 500 degrees Cent. is most striking. Compressive strength values of almost 400,000 pounds per square inch are reached, thus slightly surpassing corresponding values for hot-pressed copper (3). At the same time this hot-pressed material shows great malleability and plastic

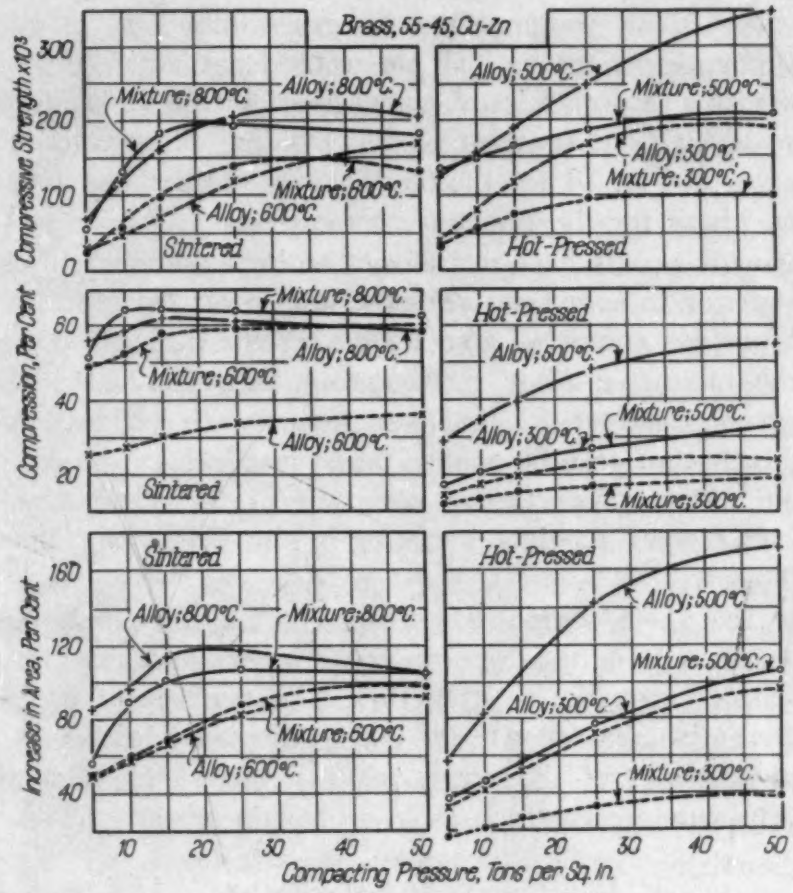


Fig. 20—Compressive Properties Versus Compacting Pressure for 55-45 Copper-Zinc Compacts.

deformability (compression and increase in area) during the compression tests with figures close to those obtained with sintered brass of the same composition. The superiority in compressive properties of the material hot-pressed at 500 degrees Cent. over that hot-pressed at 300 degrees Cent. is understandable in view of the microstructure shown in Fig. 5. The same explanation is true for the fact that pre-alloyed compacts show better results than material prepared from the powder mixture.

The general trend of the curves for the 75-25 composition (Fig. 18) follows closely the one shown and discussed in the case of the 85-15 composition. In these diagrams, too, the general tendency is maintained that compacts treated at the higher temperatures are superior to those treated at the lower temperatures, and that compacts prepared from alloy powder are also superior to material made from the powder mixture. In the case of alloy powder pressed at 500 degrees Cent. compressive strength values well in excess of 400,000 pounds per square inch are reached.

Compressive properties of compacts of the 65-35 brass composition are given as a function of the molding pressure in Fig. 19. The curves in Fig. 19 for the 65-35 composition show close resemblance to those for the previous compositions.

Again compacts heat treated at the higher temperatures prove to be superior to compacts treated at the lower temperature. Prealloyed powder compacts give better results than compacts made from the mixture. Alloy powder compacts after hot-pressing at 500 degrees Cent. at 50 tons per square inch yield compressive strength values of 450,000 pounds per square inch.

Compressive properties of compacts of the 55-45 composition are shown versus molding pressure in the diagrams a and b of Fig. 20.

For the 55-45 composition (Fig. 20) the curves show similar characteristics as in the case of the other compositions, although actual data of compressive strength and particularly of compression and increase in area are inferior due to increased brittleness. Also frequent crossings of the curves make it more difficult to observe an orderly arrangement such as is evident in previous cases.

Summary

Binary brasses with different percentages of zinc have been prepared from metallic powders. Their microstructure, density, hardness and compressive properties have been studied. The influence of certain basic factors on these properties, such as composition and type of initial powder used, or the molding procedure employed, has been investigated.

The inferiority of compacts hot-pressed from alloy powders over similar compacts made with mixed copper and zinc powders, as found by Jones, could not be affirmed. In general, compacts made

from previously alloyed powders showed a better diffused structure, and superior physical properties, both for sintered and hot-pressed material. Exceptions were density values of hot-pressed compacts of all compositions, and hardness values of hot-pressed compacts for the 55-45 composition. These were higher in the case of mixed powders as raw material.

The difference between these results and those of Jones may be explained by several reasons. Jones' experimental procedure differed considerably from that used in this investigation. He used substantially higher hot-pressing temperatures and molding pressures of the order of the lowest pressures used in this research. In addition Jones failed to experiment with protective atmospheres during hot-pressing, and probably most important of all, the alloy powder used by Jones was of an entirely different nature from the powder used here. In this investigation alloy powder was obtained by a low temperature sinter treatment in a protective atmosphere, thus producing soft annealed, plastic, and irregularly shaped powder particles of rather coarse size. Jones, on the other hand, employed alloy powders originating from entirely different sources and displaying other characteristics. The assumption, that his 300 mesh powder was obtained by mechanical pulverization of the cast ingot material, permits the conclusion that his powder was strained and rendered brittle, unless it was annealed afterwards. Such material must possess rather poor compactibility under pressure and must yield fragile compacts due to the substantial lack of contact areas between the individual particles. Although during hot pressing the powder compacts are annealed, the extent of such annealing is not made clear in Jones' paper, as no reference is made to the time that the individual compacts were kept at temperature.

However, it must be kept in mind, that in this investigation, too, some indications point towards a possible superiority of alloy compacts hot-pressed from powder mixtures. The density data of hot-pressed compacts are of particular interest in this connection. It may be safely stated that only if the alloy powder used is of great plasticity, affording ample areas of contact between the particles during pressing, can full advantage of the advanced state of diffusion be taken and optimum physical properties obtained. This holds for sintered metal as well as for hot-pressed material.

Hot-pressed brass compacts displayed physical characteristics generally superior to those obtained with sintered alloys of same

composition. Although the structure of such hot-pressed material still lacked uniformity and a continuous matrix of polygonal-shaped crystals, for high molding pressures it did not display the widespread pattern of pores as observed in the sintered alloys. Accordingly, density figures for hot-pressed compacts reached peak values closely approaching normal densities of cast or wrought brass of corresponding composition.

Hardness figures of hot-pressed compacts exceed by far similar properties of sintered brass. In the case of the lower press temperature of 300 degrees Cent., exceedingly high hardness values were obtained for either composition investigated at high pressures. These values are comparable to severely strained wrought brass, in certain cases exceeding peak data obtained previously with similarly hot-pressed copper powder compacts. It may be assumed that hardness of such compacts may still be increased considerably if finer basic powders are used, and Brinell figures of 200 for such brass may not be impossible.

Compressive strength figures also are more favorable in the case of hot-pressed material. Values of 400,000 pounds per square inch and higher were obtained, which could neither be reached by sintered brass of equal composition, nor by pure copper powders hot-pressed in the same manner. On the other hand, no distinct superiority of hot-pressed compacts over sintered compacts was obtained in the case of compression and increase in area figures, indicating that such hot-pressed brass compacts substantially lacked malleability.

If sintered metals are compared with hot-pressed compacts, the question of volumetric changes is of particular interest from a commercial viewpoint. Hot-pressed compacts practically maintained their dimensions within closest tolerances regardless of the temperature or pressure used in the work. After compression of more than two thousand compacts in the same die at temperatures up to 600 degrees Cent. and at pressures up to 50 tons per square inch the $\frac{5}{8}$-inch diameter of the resulting compacts had increased less than one thousandth of 1 inch.

On the other hand, changes in volume were found to be considerable in the case of sintered brass. Both shrinkage and growth phenomena were observed depending upon composition and treatment of the initial powders as well as on molding and sintering steps. In general, sintered brass compacts increased their volume

less if prepared from alloy powders, as most of the complex volumetric changes of the individual particles have taken place during the pre-alloying treatment. Growth of the compacts increased with rising zinc content and with compacting pressure, and was found excessive for the low sintering temperature. In the case of the highest zinc composition, increase in volume approached as much as 50 per cent.

Weight changes observed during sintering were found to be not so marked, although they amounted in certain cases to 10 to 15 per cent. Both weight gains and losses were observed, depending again on factors similar to those which influenced the volumetric changes. Gas adsorption and evolution, diffusion, sintering and gravity forces, as well as zinc losses due to evaporation, may be considered the chief factors in causing these unwanted changes in volume and weight.

Molding pressure and heat treating temperature affects the structure and properties of brass compacts much the same way as in the case of pure copper. Rising molding pressures cause consolidation of the structure, both in the case of sintered and hot-pressed material. In most cases physical properties rise hyperbolically with increasing molding pressures and reach peak values at the high pressures.

The higher heat treating temperature generally causes advanced crystallization and diffusion and, accordingly, higher density and physical properties. The only exception is hardness data of compacts hot-pressed at very high pressures. Here the material hot-pressed at 300 degrees Cent. was found to be harder, probably on account of its strained condition at a temperature slightly below the recovery temperature range. These observations were found to be in close agreement with tests made on pure copper.

Diffusion of the two metals is much dependent on the treatment to which the compacts are subjected. Certain observations made during this work are in close agreement with Owen and Pickup's investigation. Alloying attempts by sintering a powder mixture at 450 degrees Cent. (840 degrees Fahr.), just above the melting point of zinc, were found to be only partly successful. It may be assumed that complete diffusion may be obtained only at treatments above 600 degrees Cent. (1110 degrees Fahr.). On the other hand, there is a possibility that certain completely alloyed powders may be more difficult to compress either cold or hot, due to increased resistance of

the material to plastic deformation, thus causing porous and weak compacts with qualities closer to those reported by Jones.

High temperature sinter treatments promote complete diffusion and the formation of a homogeneous alpha solid solution up to the 65-35 composition, the only difference from normal brass of similar composition being the abundance of microscopic pores. In hot-pressed material, on the other hand, diffusion was not quite as advanced; first because of the much lower heat treating temperatures, and secondly because of the short time during which the compacts were subjected to the press temperature.

The composition of the brass compacts also has its influence on structure and properties. In the case of sintered compacts the structure does not disclose unexpected phases; in hot-pressed compacts, however, incomplete diffusion often causes transitory, copper-rich areas or zinc-rich phases to remain in part. This is particularly true for compacts hot-pressed from the powder mixture, and has some bearing on the physical properties. Most striking is the case of the 55-45 composition, where hot-pressed compacts prepared from the mixed powders show an extreme hardness, which can only be explained by the presence of a brittle, hard, zinc-rich phase in great proportion, as confirmed by the microstructure.

The change in composition has certain effects on the physical properties tested. Density decreases with increasing zinc content under otherwise identical conditions. Hardness, on the other hand, rises for hot-pressed material, while it generally drops for sintered material due to gross increase in porosity. Compressive strength values reach peaks at the 65-35 composition, after which they fall off. Malleability figures, such as compression, steadily decrease with increasing zinc content, as may be expected due to growing brittleness.

In conclusion it may be stated that the powder metallurgy of brass offers a wide and interesting field of work with good prospects of results. The fact that sintered brass compositions are subject to dimensional changes probably constitutes a major handicap in the development of such materials along industrial lines today. As shown in this paper, control of dimensional changes is not easy in the case of sintered brass and requires careful planning and close control of numerous processing steps. However, there is reason to believe that for certain specific applications sintered brass may have definite possibilities.

Results obtained with hot-pressed brass powder compacts are very encouraging. Aside from the fact that dimensions can be controlled much more closely, commercial alloys, especially of higher zinc content (such as Muntz metal, etc.), due to their great plasticity at elevated temperatures are ideally suited for hot pressing operations at commercial pressures and temperatures between 400 and 600 degrees Cent. (750 and 1110 degrees Fahr.). The use of previously alloyed powders constitutes an additional aid, particularly if low press temperatures are to be used, but is not always essential or even desirable.

Acknowledgments

The author is grateful to the American Electro Metal Corporation for permission to publish these results. Appreciation is given to Mr. George Stern for the preparation of the photomicrographs.

Bibliography

1. C. G. Goetzel, "Powder Metallurgy of Copper", *Metals and Alloys,* Vol. 12, No. 1 and 2, 1940, p. 30 and 154.
2. C. G. Goetzel, "Structure and Properties of Copper Powder Compacts", *Journal,* Institute of Metals, Vol. 66, Part 9, 1940.
3. C. G. Goetzel, "Some Properties of Hot-Pressed and Sintered Copper Powder Compacts", TRANSACTIONS, American Society for Metals, Vol. 28, 1940, p. 909.
4. W. D. Jones, "Hot Pressing of Metal Powders", *Metal Industry,* London, March 1940, p. 225.
5. W. D. Jones, "Powder Metallurgy", *Metal Industry,* London, Jan. 1940, p. 69.
6. E. A. Owen and L. Pickup, "X-ray Study of Interdiffusion of Copper and Zinc", *Proceedings,* Royal Society, London, A 149, 1935, p. 282.

DISCUSSION

Written Discussion: By E. I. Larsen, division engineer, and F. H. Vandenburgh, metallurgical engineer, Alloy Engineering Division, P. R. Mallory & Co., Inc., Indianapolis.

Because of the increasing interest in, and importance of powder metallurgy as a means for manufacturing finished or semi-finished products, the paper by Dr. Goetzel is of great value and interest to those engaged in this art.

In this discussion of Dr. Goetzel's paper the following points will be commented upon: 1. Processing and testing. 2. Compressive value. 3. The comparison of hot-pressed compacts to sintered compacts. 4. Confirmation that alloy powders usually yield better compacts than do powder mixtures.

It is felt that Dr. Goetzel's paper would be of more value if a detailed description of the equipment and procedure was included. Many pages are given over to test results which do not mean a great deal unless the reader looks up a previously published paper and its subsequent discussion. This is also true of the section on compressive strength. In the usual engineering sense, a compressive strength of 400,000 pounds or more is surely unusual for any copper-base alloy. If the compressive strength were given as a per cent length change or as a defined yield point, it would mean more and would lend itself to comparison much more readily.

Dr. Goetzel has presented data to show that hot-pressed brass compacts display physical characteristics generally superior to those obtained with sintered alloys of the same compositions. This can be agreed with insofar as Dr. Goetzel has gone. It is known, however, and was brought out by Dr. Goetzel in his paper on "Hot Pressing of Iron Powder", that properties greatly superior to those used by Dr. Goetzel for comparison purposes, can be obtained by repressing and resintering, and, in some instances, repressing alone. This can be brought out by comparing the properties obtained on test bars made by sintering, of 200 mesh 70-30 brass alloy powder with the properties obtained by Jones in his work on the hot pressing of binary brass compacts.

Table IA

	Tensile Strength (psi.)	Per Cent Elongation	Brinell Hardness	Source
Pressed, Sintered, Repressed, Resintered and Repressed 70-30 Brass Alloy Powder	38,400	15.2	80	P. R. Mallory & Co., Inc.
Hot-Pressed 70-30 Brass Alloy Powder	30,000	21.0	..	Jones
Hot-Pressed 70-30 Powder Mixture	38,000	16.0	114	Jones

It is interesting to note how closely the physical properties of the sintered brass compacts correspond to the values Jones obtained by hot pressing the powder mixture.

Other sintered 70-30 brass test pieces produced by pressing, sintering, repressing, resintering, repressing, and cold rolling 20 per cent, display the physical properties listed in Table IIA.

Table IIA

	Tensile Strength (psi.)	Per Cent Elongation	Brinell Hardness	Source
Pressed, Sintered, Repressed, Resintered and Repressed Cold Rolled 20 Per Cent 70-30 Brass.	60,500	3.2	125	P. R. Mallory & Co., Inc.
Same as above, except strain relieved	48,000	24.8	120	P. R. Mallory & Co., Inc.

At present, with hot pressing still in the laboratory or pilot plant stage, its practical application is somewhat limited. With this in mind, it is felt that consideration should be given to the properties obtainable by pressing, sintering and repressing and, if necessary, resintering. These extra operations, involving in certain cases different compacting and repressing dies, add to the cost. However, it is believed that the cold pressing and sintering procedure, in many cases, may be more economical than hot pressing with its expensive, bulky equipment, plus high die costs.

Also, cold pressing is readily adaptable to automatic presses, whereas, hot pressing can be used only rarely and with difficulty in automatic presses.

It is with pleasure that Dr. Goetzel's statement, "The use of alloy powders leads to better properties—" can be verified not only with brass but also with bronze.

Physical Properties of Sintered Bronze*

	Mixture of Powders		Alloy Powder	
	As Repressed	Annealed	As Repressed	Annealed
Ultimate Tensile Strength, psi...	46,250	35,000	48,600	41,000
Per Cent Elongation in 2 Inches.	0.8	5.0	1.6	8.0
Hardness, Rockwell B	51	36	61	38
Impact (Square Bar)	6 ft.lbs.	20 ft.lbs.	38 ft.lbs.	100 ft.lbs.

*Source—P. R. Mallory & Co., Inc.

The tensile data were obtained on standard 0.505-inch diameter test bars machined from compacts which had been prepared by pressing, sintering and repressing.

Written Discussion: By D. C. Jillson, research division, The New Jersey Zinc Company (of Pa.), Palmerton, Pa.

The data presented by Dr. Goetzel make an interesting and worthwhile contribution to a field where the amount of published information is, as yet, extremely meager. It is regrettable, however, that he was unable to determine properties other than hardness and compressive strength. Tensile strength, impact strength, bending, and ductility are of particular importance and information concerning the influence of processing variables on these properties as well as on hardness and compressive strength would increase the value of this contribution considerably.

It seems probable that hot pressing of brass powders will have certain advantages over cold pressing and sintering methods, but the few properties on which data are presented in this paper hardly justify the conclusion that "hot-pressed brass compacts displayed physical characteristics *generally* superior to those obtained with sintered alloys of the same composition". The question might also be raised whether optimum conditions were used in the preparation of either the hot-pressed or the cold-pressed and sintered specimens.

Regarding changes of dimensions of cold-pressed compacts upon sintering, it hardly need be pointed out that in many cases it is feasible to allow for this in designing the die. Moreover, there are cases where changes of dimensions during sintering have been made negligible by proper choice of conditions. It seems probable that much more can be done in this direction as our knowledge of the effects of the variables involved increases.

A few comments on some of the details of Dr. Goetzel's technique may be of use to other investigators. Treatment of mixed copper and zinc powders in commercial hydrogen at 275 degrees Cent. (525 degrees Fahr.) will not reduce zinc oxide. Also, Dr. Goetzel's diffusion treatment of two hours at 450 degrees Cent. (840 degrees Fahr.) in hydrogen could not be expected to produce homogeneous alpha brass from mixed copper and zinc powders. The rate of interdiffusion of copper and zinc to form homogeneous alpha brass is much slower than is generally realized.

In discussing the growth of compacts of mixed copper–and zinc powders when sintered in hydrogen, the author did not mention specifically the fact that copper adsorbs large quantities of hydrogen, whereas the adsorption by brass is generally considered much smaller. This suggests, as one of the possible causes for growth, the adsorption of hydrogen by the copper and its re-evolution when the copper alloys with the zinc.

Written Discussion: By Joseph E. Drapeau, Jr., technical director, Metals Refining Co., Hammond, Ind.

Why should Dr. Goetzel present such a paper before this society? I'll tell you why, simply because he is a research man who has taken a deep interest in this rapidly developing field of powdered metallurgy. For instance, he realizes that his test data will require many practical considerations by you men experienced in this field. He recognizes the fact that any research that may just indicate or suggest improvements in the art of powdered metals, such as physical properties of the powders or reduction in cost, are in continual demand in our economic system.

Our laboratory confirms most of the facts brought out in Dr. Goetzel's paper. We find in every case that the higher the molding pressure, the greater the sintering growth, the greater the density of the compressed and sintered powders, and the harder the final product when all the factors, such as the type of powder or powders, temperature and sintering conditions, are equal.

We believe the interest and value of Dr. Goetzel's paper might possibly be improved if he had shown more data relative to the particle size and particle size distribution, the compressibility standards, apparent density and mobility of the powders and alloy powders that he employed in his work. Are we correct, Dr. Goetzel, in assuming that all the mixtures of copper and zinc that were compressed were made from the same batch of powder? You pointed out that the prepared alloys of these powders gave a coarser powder. We have made rather extensive investigations over the past ten years on this one item of particle size and particle size distribution and its effect upon green growth, sintering growth, apparent density, mobility, etc. In every case we find that the particle size of the powder reflects itself in the characteristics of the compressed and sintered product.

I believe the introduction of alloy powders will increase the cost of the metal powders to the consumer, and I know the producers of these alloy powders will be required to supply the consumer with powder of uniform chemical and physical characteristics.

We confirm your findings that alloy powders are harder to compress than mixtures of the same powder unalloyed. It is quite possible that these alloy powders may introduce problems of die wear. Can this die wear be overcome

through hot pressing? Will it enable you to employ smaller presses for the same finished product?

It is my personal opinion that your paper covers a field of powdered metallurgy that is limited in application. Its future may depend upon the ability of the engineer and metallurgist to produce cheaper alloy powders and to overcome some of the problems that the introduction of hot pressing may bring out. Let us mention the problems of metal creep of a hot die, limitation of the shapes that could be pressed, problems in feeding powders to the die and atmosphere control surrounding the die. I understand some of the powdered metallurgists in large scale productions have their hands full of problems with the simple cold pressing and sintering of unalloyed metal powders.

We look forward, Dr. Goetzel, to hearing more about your research work in this new field of powdered metallurgy at future meetings of our society.

Oral Discussion

WILSON N. PRATT:[1] A lot of credit is due Dr. Goetzel for his work on the hot pressing of metal powders. It is a well known fact that products made by the cold press method have low strength, ductility, elongation and density unless they are repressed and resintered several times. This paper points the way toward better physical properties by a process called hot pressing. Apparently, metal powders may be hot-pressed to very nearly the densities and strengths of cast wrought materials. It is encouraging to note that Dr. Goetzel got 2000 pieces from a die without appreciable dimensional change. It would seem that hot-pressed products could be made directly to close tolerances as far as size and shape are concerned and that materials could be used which would give these products unique properties of their own.

In this paper, Dr. Goetzel finds he does not get excellent diffusion of zinc into copper until he reaches a temperature of 650 degrees Cent. (1200 degrees Fahr.). He could undoubtedly have improved his hot-pressed compacts by going higher than 500 degrees Cent. (930 degrees Fahr.) for his pressing temperature. There is no doubt that a higher temperature would lead to a more uniform product and, in fact, it is my experience that with higher temperatures the origin of the powders becomes less important.

It is inadvisable to use hydrogen as a protective atmosphere when working with brass powders. In a thesis written by William P. Goepfert for his Master's Degree at the Polytechnic Institute of Brooklyn, he found while working with brass powders of 60 per cent copper-40 per cent zinc that sintering in hydrogen resulted in dezincification. At 850 degrees Cent. (1560 degrees Fahr.), 20.2 per cent of the zinc was lost. Using an atmosphere consisting of a mixture of two parts carbon dioxide and one part hydrogen by volume, there was no zinc loss.

Author's Reply

May I express my sincere appreciation for the fine contributions made during this discussion.

Mr. Vandenburgh's criticism of the lack of a detailed description of the equipment and procedure used is fully understood. However, economy in

[1]Metal Powder Laboratory, Stevens Institute of Technology, Hoboken, N. J.

space made it necessary to refer to the previous publication. In this previous publication reasons were advanced for the limitation of testing procedure and data. It is fully realized that density, hardness and compressive strength figures are only the beginning of a thorough investigation necessary on this newly developed material. The value of tensile strength, impact strength and ductility data is fully appreciated and, at the present, arrangements are being made to investigate these properties. They will be reported in a future publication.

Mr. Jillson is quite correct in criticizing the term "generally" in the statement that hot-pressed brass compacts displayed physical characteristics superior to those obtained with sintered alloys of the same composition. This statement is, of course, only correct under the experimental conditions observed in this paper which may not be the optimum conditions obtainable. However, to find such optimum conditions may call for a much more extensive research program than covered by this investigation.

The fact that a 2-hour diffusion treatment at 450 degrees Cent. (840 degrees Fahr.) in hydrogen could not produce homogeneous alpha brass from mixed copper and zinc powders was observed and taken into consideration. A higher temperature must be chosen if a perfect diffusion treatment is desired. However, there is a temperature limit in this treatment as the powder particles show a distinct tendency to sinter above 500 degrees Cent. (930 degrees Fahr.). Such sintering would then require subsequent pulverizing which may cause distortion of the individual particles.

Mr. Jillson rightfully states that copper adsorbs large quantities of hydrogen, whereas the adsorption by brass is generally considered much smaller. This may possibly be one of the reasons for growth as the adsorption of hydrogen by the copper and its re-evolution when the copper alloys with the zinc is known. This point covered in this paper by one of the three explanations given for the changes in volume during sintering.

Mr. Drapeau is quite correct in assuming that all the mixtures of copper and zinc that were compressed were made from the same batch of powder. The slight coarsening of the alloyed powder was due to initial sintering during the diffusion treatment.

The properties of copper and zinc were approximately as follows:

	Copper Per Cent	Zinc Per Cent
Through 100 on 150 mesh	5	..
Through 150 on 200 mesh	18	10
Through 200 on 250 mesh	2	5
Through 250 on 325 mesh	25	25
Through 325 mesh	50	60
Apparent density	2.5 grams per cubic centimeter	2.5 grams per cubic centimeter

The difficulty in hot pressing as mentioned by several of the contributors to this discussion are, of course, fully realized. They are the main reason that this special branch of the field is not yet very advanced. This is particularly true with regard to the problem of temperature of hot pressing. The limited hot strength of almost all metallic dies puts a decisive limit on hot pressing temperatures. In addition the problem of die wear must be considered. Mr. Pratt emphasizes the fact that the die used for these hot pressing experiments

has withstood more than 2000 compressions without appreciable wear. Although this is true, one has to realize that these 2000 compressions were made with powders of different plasticity, at many different temperatures and, ranging from 100 to 600 degrees Cent. (210 to 1110 degrees Fahr.) and at many different pressures varying from 1 to 50 tons per square inch. For this reason one cannot generalize that a high speed steel die would yield similarly satisfactory compacts if both temperature and pressure were maintained constant, say at 500 degrees Cent. (930 degrees Fahr.) and 50 tons per square inch respectively.

The statement made during this discussion that high hot pressing temperatures, preferably about 500 degrees Cent. (930 degrees Fahr.) are most advantageous from the standpoint of diffusion, can naturally not be denied. However, when deciding on the proper industrial procedure for hot pressing of brass powders, questions of die design and strength must also be considered and may well be the deciding factors, while questions of physical properties may be considered secondary.

In this connection also the question of die wear during pressing of alloy powders deserves attention. Mr. Drapeau's questions as to whether die wear could be overcome by hot pressing and also as to whether smaller presses could be employed for the same finished product if pressing is done at elevated temperatures can both be answered in the affirmative.

Mr. Pratt brought up the interesting question of the heat treating atmosphere. It is known that hydrogen, as a protective atmosphere when working with brass powders, is not an ideal condition. Mr. Pratt's reference to a sintering atmosphere for brass, consisting of a mixture of two parts carbon dioxide and one part hydrogen, is therefore of particular interest and deserves further studying.

Finally, a few comments should be made on the contributions by Messrs. Larsen and Vandenburgh. The data presented by these gentlemen are very interesting indeed, and it is noted with appreciation that these gentlemen also found that alloy powders yielded superior properties in the final compacts. Of course, as mentioned in the conclusions of this paper, the history of these alloy powders has an important bearing on the properties.

It is realized that sintered brass may, under certain circumstances possess physical properties equal or superior to those obtained by hot pressing. Such comparisons are justified only if the experimental or industrial conditions encountered are considered. If for reasons of strength, hot pressing temperatures must stay relatively low, optimum values of physical properties cannot be reached. Sintered brass compacts made by conventional powder metallurgical methods, such as cold pressing, sintering, repressing and annealing, may then be superior. This superiority may still be improved by repeated cold pressing and sintering operations, such as indicated by Messrs. Larsen and Vandenburgh. On the other hand, cold repressing at high pressures after sintering causes considerable die wear especially if the metal is not very plastic. This and the fact that a multitude of operations may be necessary for the molding and heat treatment of one piece may render the entire process of making sintered brass parts industrially uneconomical.

THE PRECIPITATION REACTION IN AGED COLD-ROLLED BRASSES: ITS EFFECTS ON HARDNESS, CONDUCTIVITY, AND TENSILE PROPERTIES

By R. H. Harrington and T. C. Jester

Abstract

As previously reported for the case of phosphor bronze, (1) (2)[1] aging below recrystallization temperatures results in a combined increase in elastic properties, elongation, fatigue resistance, and electrical conductivity for the cold-rolled brasses. Data are given for the commercial 85-15 and 65-35 brasses in two conditions of cold work: 4 numbers hard and 8 numbers hard. Precipitation aging, induced by the presence of cold-work strain, explains the deviation of the actual hardness-temperature curve from the theoretical curve for simple recrystallization.

Introduction

"IT is well known that the first effect of annealing cold-worked brass is a slight hardening." This statement appears in "Science of Metals" by Jeffries and Archer, (3). Several references therein (4), (5), (6), (7) record various increases in tensile properties when cold-rolled brass was aged at temperatures below those resulting in recrystallization. Thus the following observation from data given by Moore and Beckinsale (6) is typical: "Heating cold-worked brass for one hour at 250 degrees Cent. (480 degrees Fahr.) practically doubled the proportional limit." In more recent research reports (8), (9), (10), (11) further data of this type are recorded coincidentally to other research objectives. In view of marked improvements in testing methods during the past twenty years, and in consideration of new knowledge and theories (1), (2), these apparent anomalies assumed real significance; and a study of the aging effects in cold-rolled brasses became both logical and mandatory.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. Of the authors, R. H. Harrington is research metallurgist, and T. C. Jester is research assistant, General Electric Co., Schenectady, N. Y. Manuscript received July 22, 1941.

Material

Two commercial brasses form the basis for this report, (1) 85 copper-15 zinc and (2) 65 copper-35 zinc. Each of these compositions, in the form of 40-mil strip one inch wide, was tested in two degrees of cold work, "4 numbers hard" (37 per cent cold reduction) and "8 numbers hard" (60 per cent cold reduction). The materials were of normal grain size, characteristic of commercial products. It has previously been shown (2) that marked variation in grain size produced only minor variations in the aging effects.

Tests

The tests resolved themselves into the following successive steps:

1. Determination of the temperature-hardness recrystallization curves. Separate samples of each grade of material were heated for 4 hours at each selected temperature. Critical aging temperatures were selected from these data, and the effect of time was determined for 10-hour and 100-hour treatments. Rockwell B hardness tests were made, with the exception of aging temperatures above 325 degrees Cent. (615 degrees Fahr.) when Rockwell F tests were translated to the B scale. Results are averages of ten or more readings. Since new samples were used for each aging treatment, cumulative (or "double") aging was avoided.
2. Determination of the maximum aging temperature (without undue loss of hardness) in the cold-rolled materials for extended periods of time.
3. Effect of strain and aging temperature on the electrical conductivity as compared to conductivity of material as received in the cold-rolled state and after complete recrystallization.
4. Effect of the induced precipitation reaction on the tensile properties. The proportional limits were measured by means of a Sayre extensometer with an accuracy of 1 part in 100,000. The elastic limits were determined with the Sayre extensometer as the stresses required to produce a permanent elongation of 1 to 2 parts in 100,000. Each tabulated result is the average for three standard tensile test samples.
5. Effect of the induced precipitation reaction on the endurance properties.
6. Photomicrographs of the material in the various conditions.

Temperature Hardness Recrystallization Curves

Some new principles affecting recrystallization have been suggested (1) and demonstrated relative to the aging of cold-rolled phosphor bronze (2).

There are two types of strain to be considered in a cold-worked, solid-solution alloy, (a) "elastic strain" and (b) "plastic strain". By "elastic strain" is meant the lattice distortion which is relieved by

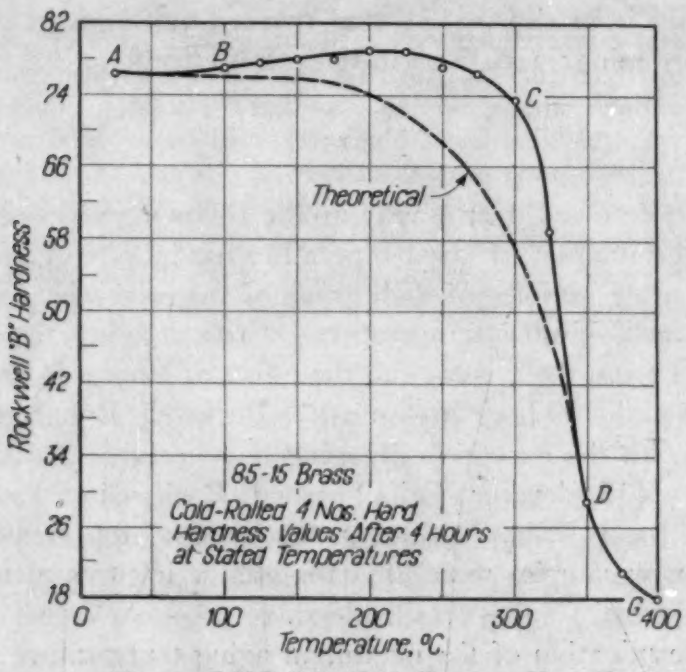


Fig. 1—Cold-Rolled 85-15 Brass 4 Nos. Hard. Hardness Values After 4 Hours at Stated Temperatures.

restoration diffusion. By "plastic strain" is meant the crystal distortion which is relieved only by recrystallization. Thus, in cold-worked metals or solid-solution alloys, heating for a relatively short time at temperatures below the "recrystallization temperature" will effect relief from elastic strain with little or no effect on the plastic strain.

The temperature-hardness recrystallization data for 4-hour aging periods are given in Figs. 1, 2, 3, and 4 for the 85-15 brass, 4 and 8 numbers hard, and for the 65-35 brass, 4 and 8 numbers hard, respectively.

As previously reported (1), (2), if the recrystallization is simply the relief of plastic strain, the temperature-hardness recrystallization curve should be of the probability type with normal distribution of

local areas according to the degree of strain. Thus those few areas of the highest plastic strain will recrystallize at lowest temperature, etc.

The resulting probability temperature-hardness relationship is indicated by the "theoretical" curves (broken line) drawn in Figs. 1, 2, 3, and 4. The effect of increased plastic strain is to both induce

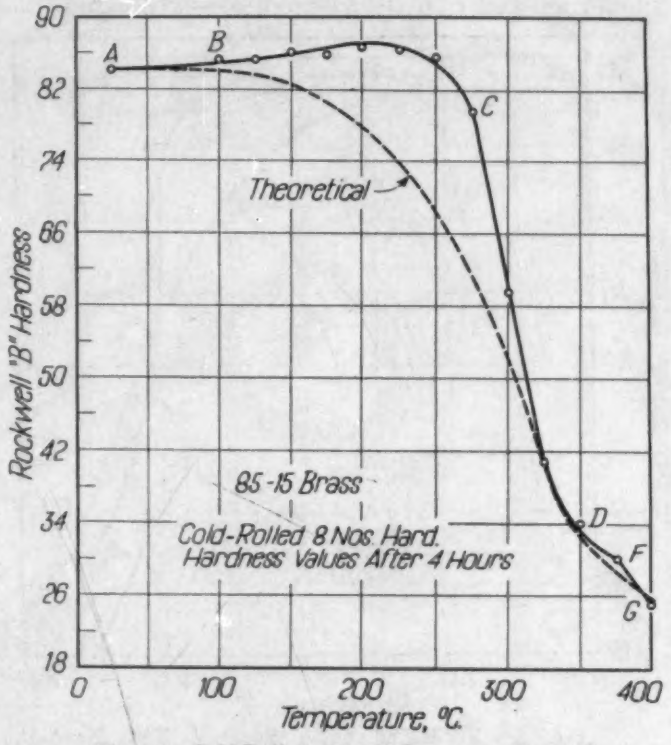


Fig. 2—Cold-Rolled 85-15 Brass 8 Nos. Hard. Hardness Values After 4 Hours at Stated Temperatures.

slightly greater aging hardness and to lower the temperature for maximum age hardening. The present data for the brasses show also that increase in alloy (solute) content produces similar effects. Also, for the same degree of plastic strain, the induced aging effects are more pronounced than for cold-rolled phosphor bronze (2), probably because of the greater solute (zinc) content in the brasses.

A. The Theoretical Recrystallization Curve. The broken-line curve represents the recrystallization of cold-worked solid-solution brass were it not susceptible to precipitation when reheated under conditions of plastic strain, and neglecting the early relief from elastic strain. Thus, from A to G, recrystallization from plastic strain would occur with no precipitation effects.

B. Actual Recrystallization Curve. The solid-line curve repre-

sents the actual data for the specific temperature-hardness recrystallization reaction. The range from A to B shows relatively no change in hardness and probably involves only slight relief of elastic strain. From B to C the hardness actually increases to a maximum between B and C, indicative of precipitation effects. From C to D, the hardness drops with abnormal rapidity as re-solution occurs with

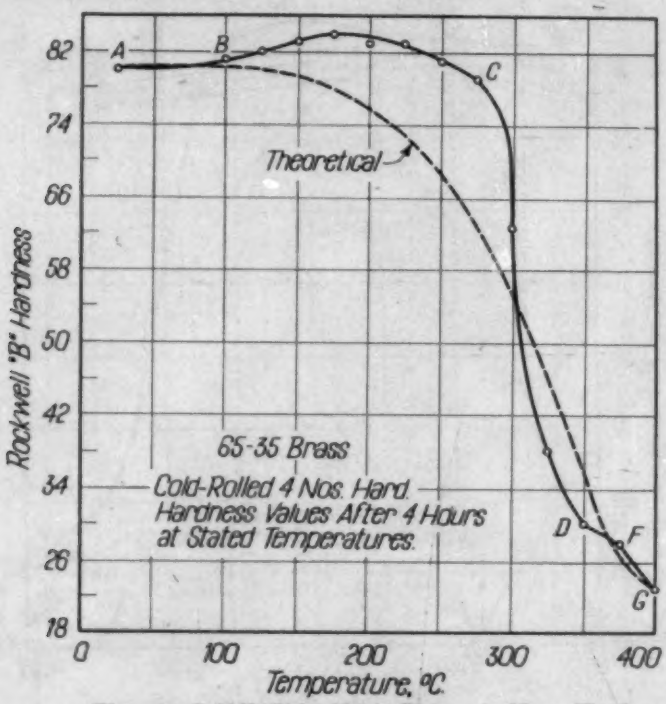


Fig. 3—Cold-Rolled 65-35 Brass 4 Nos. Hard. Hardness Values After 4 Hours at Stated Temperatures.

consequent elimination of the precipitated phase as an agent blocking the diffusion necessary for recrystallization. With release from this blocking effect, the internal energy content of the system at temperatures in the range from C to D causes recrystallization to proceed in this range at an abnormally high rate. This, in turn, results in hysteresis effects at D to F, deviations from the theoretical effect. As should be expected, these hysteresis effects are more pronounced with increase in plastic strain and with increase in solute element content. The effects of the induced precipitation reaction are apparently eliminated at G; and, above 400 degrees Cent. (750 degrees Fahr.) by all reports, the hardness-temperature curves are normal, the hardness decreasing with the coarsening of grain size at further elevated temperatures.

Temperature, Time, Hardness Effects

The effects of 4-hour aging periods on the hardness for temperatures below recrystallization have been described in detail in Figs. 1, 2, 3, and 4 and are conveniently summarized in Fig. 5 for the 85-15 brass and in Fig. 6 for the 65-35 brass. Age hardening is definitely established, increasing with increase in plastic strain and

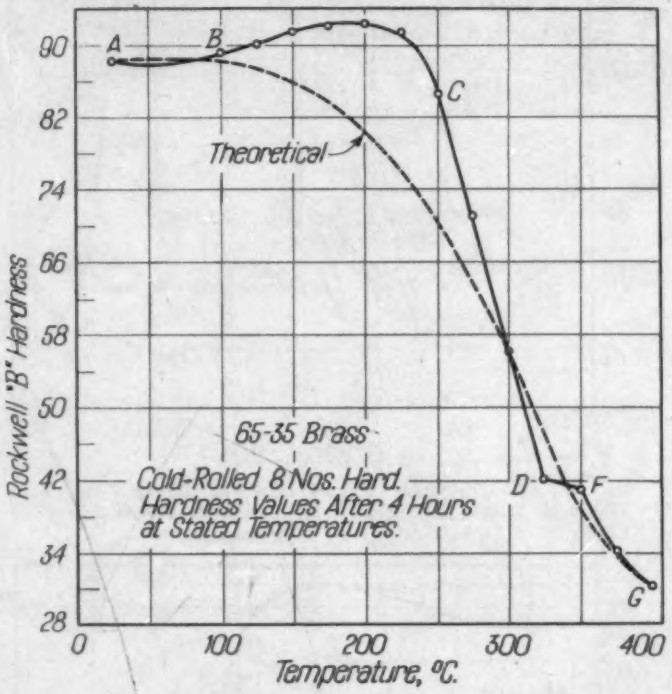


Fig. 4—Cold-Rolled 65-35 Brass 8 Nos. Hard. Hardness Values After 4 Hours at Stated Temperatures.

especially with increase in solute content. Initiation of true recrystallization takes place at lower temperatures with increase in plastic strain and increase in solute content. Completion of recrystallization, however, takes place at higher temperatures for increase in plastic strain and increase in solute content. The hardness during these last stages appears to be affected by two factors, (a) hysteresis, and (b) actual grain sizes resulting from the preceding recrystallization.

The effects on hardness of increasing the aging time at the constant temperatures of 150, 175, 200, and 225 degrees Cent. (300, 345, 390 and 435 degrees Fahr.) are shown in Figs. 7, 8, 9, and 10, respectively.

The precipitation reaction is about 90 per cent complete after 10 hours at 150 degrees Cent. (300 degrees Fahr.) and is not quite

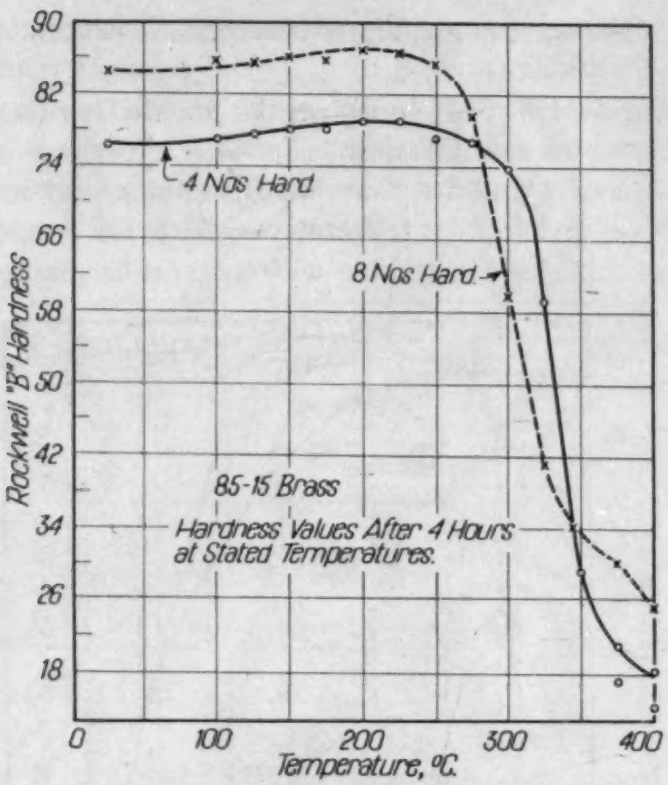


Fig. 5—Hardness Values of 85-15 Brass After 4 Hours at Stated Temperatures. Circle = 4 Nos. Hard, Cross = 8 Nos. Hard.

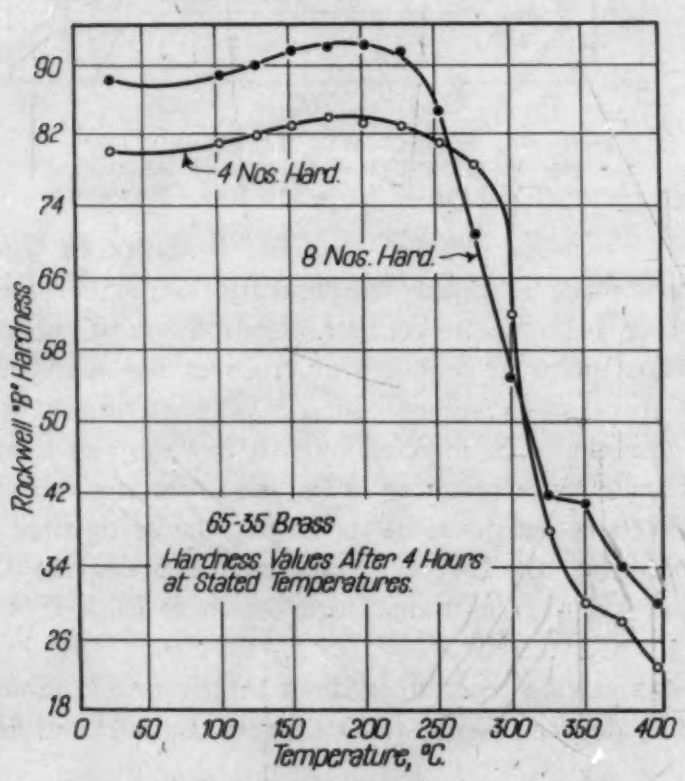


Fig. 6—Hardness Values of 65-35 Brass After 4 Hours at Stated Temperatures. Circle = 4 Nos. Hard, Cross = 8 Nos. Hard.

complete after 100 hours at this temperature. For engineering service at this temperature, these brasses should be "stabilized" by a 10-hour aging treatment at 150 degrees Cent. (300 degrees Fahr.).

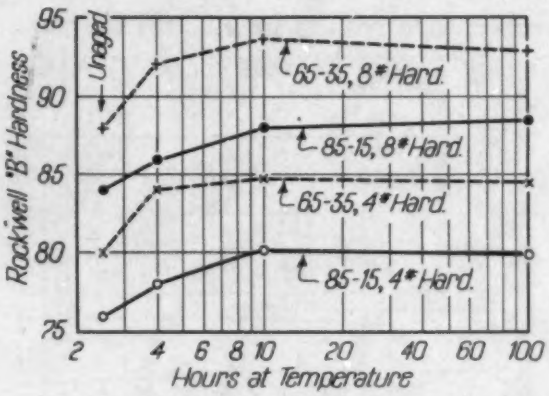


Fig. 7—Effect of Time on Brasses Aged at 150 Degrees Cent.

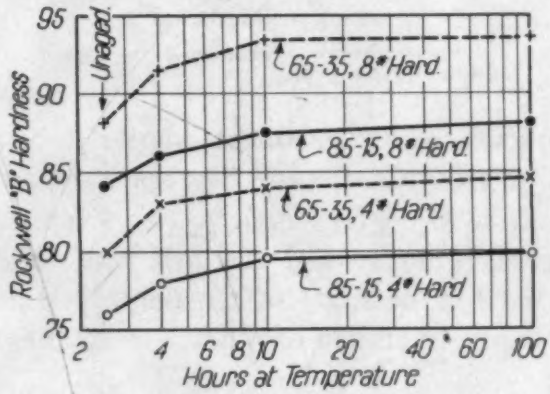


Fig. 8—Effect of Time on Brasses Aged at 175 Degrees Cent.

The precipitation reaction is practically complete after 10 hours at 175 degrees Cent. (345 degrees Fahr.) with practically no change in hardness with further time at this temperature (up to 100 hours). For engineering service at this temperature, a "stabilizing" treatment of 10 hours at 175 degrees Cent. (345 degrees Fahr.) is recommended (previous to assembly). The maximum service temperature for these brasses for long extended periods is 175 degrees Cent. (345 degrees Fahr.).

The precipitation reaction is about 90 per cent completed after 4 hours at 200 degrees Cent. (390 degrees Fahr.) and appears to be completed within 10 hours' aging. Further heating up to 100 hours shows a general tendency for slight overaging with the 65-35 brass,

8 numbers hard, actually softening to a hardness slightly below that of the as-rolled condition.

The precipitation reaction is practically completed after 4 hours at 225 degrees Cent. (435 degrees Fahr.). Time in excess of 10 hours at this temperature results in a slight increase in overaging as compared with aging at 200 degrees Cent. (390 degrees Fahr.).

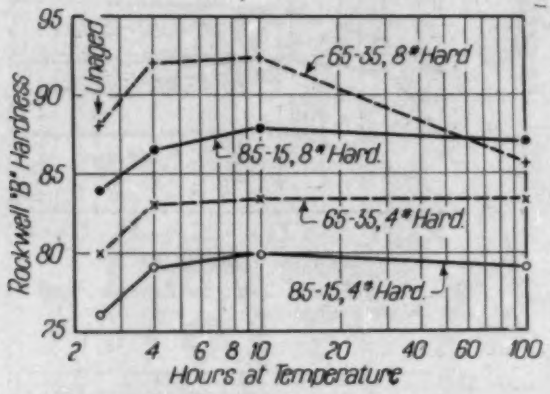


Fig. 9—Effect of Time on Brasses Aged at 200 Degrees Cent.

Thus the practical aging treatments appear to be as follows: (a) 10 hours at 175 degrees Cent. (345 degrees Fahr.), (b) 4 hours at 200 degrees Cent. (390 degrees Fahr.), (c) 4 hours at 225 degrees Cent. (435 degrees Fahr.); and the first two of these were the treatments selected for the study of tensile properties, together with the slightly over-aging treatment of 4 hours at 250 degrees Cent. (480 degrees Fahr.).

Quite clearly, 175 degrees Cent. (345 degrees Fahr.) develops the maximum age hardening for a 10-hour aging period. (Fig. 11).

It is apparent that 175 degrees Cent. (345 degrees Fahr.) is the maximum service temperature for these materials with very slight overaging taking place in the material of greatest strain, the 65-35 brass 8 numbers hard. For periods of more than 100 hours at elevated temperatures, it might be best to limit the service temperature to 150 degrees Cent. (300 degrees Fahr.) for the most consistent performance (in the case of springs, for example). (Fig 12).

The Effect of Strain and Subsequent Aging on Electrical Conductivity

Table I shows the aging effects on the electrical conductivities

of the 85-15 brass, 4 and 8 numbers hard, and the 65-35 brass, 4 and 8 numbers hard, respectively. The variation of conductivity with aging treatments applied to a cold-worked, solid solution alloy has been previously described (2) with considerable detail. The present

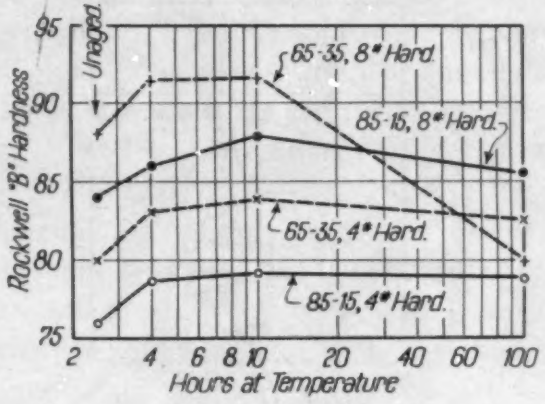


Fig. 10—Effect of Time on Brasses Aged at 225 Degrees Cent.

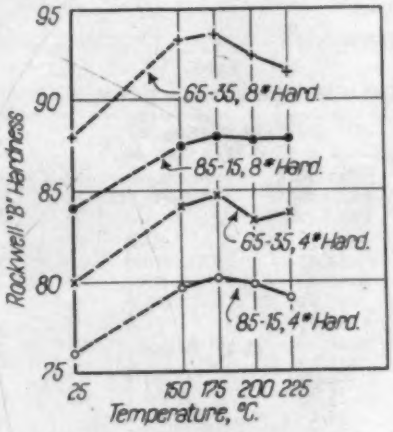


Fig. 11—Effect of Temperature on Brasses With Constant Time of 10 Hours.

tables for the brasses compare the results of the three derived practical treatments with the conductivities for the annealed and cold-rolled conditions. Hardness values are also included so that it may be readily seen that the conductivity versus hardness data appear to be the criteria for establishing the involved reaction as one of precipitation.

For these pre-recrystallization treatments, both the conductivity and the hardness values show definite increases over the values for the as-rolled conditions. If the hardness increase could be due

in some way to an increase of strain, it is definitely known that the conductivity should have decreased, contrary to the established data. Conversely, if the increase in conductivity was due in large part to the relief of strain alone, the hardness should have decreased. Hence

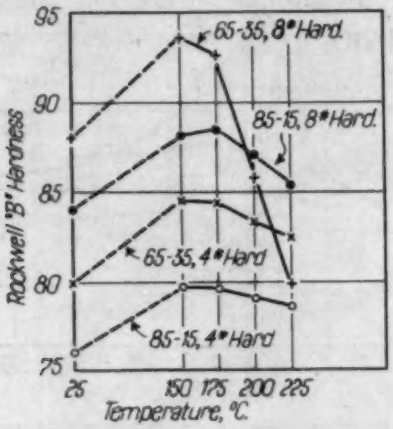


Fig. 12—Effect of Temperature on Brasses With Constant Time of 100 Hours.

Table I
Effect of Aging on Electrical Conductivity of 85-15 and 65-35 Brass

Treatment	4 Nos. Hard — Electrical Conductivity Per Cent	4 Nos. Hard — Rockwell B	8 Nos. Hard — Electrical Conductivity Per Cent	8 Nos. Hard — Rockwell B
85-15 Brass				
Annealed	36.5	Soft	36.4	Soft
Cold-Rolled	34.6	76.0	34.0	84.5
10 Hrs. 175° C.	35.4	80.1	34.7	88.0
4 Hrs. 200° C.	35.5	79.0	35.0	86.7
4 Hrs. 250° C.	35.6	77.0	35.2	85.2
65-35 Brass				
Annealed	27.3	Soft	27.4	Soft
Cold-Rolled	25.8	80.2	24.6	88.4
10 Hrs. 175° C.	26.4	84.7	25.7	93.6
4 Hrs. 200° C.	26.4	83.0	25.7	92.0
4 Hrs. 250° C.	26.5	81.0	26.2	84.5

it seems rather well established that the induced reaction is one of precipitation.

Effect of Strain and Subsequent Aging on the Tensile Properties

Table II shows the effects on the physical properties, including tensile properties, for the 85-15 brass for each of the two conditions: 4 numbers and 8 numbers hard. Again, as for the phosphor bronze (2), increases in the elastic properties are combined with an increase

in elongation (with two exceptions for the 4 numbers hard material wherein decreases in elongation as compared to the as-rolled condition are in line with properties to be expected from a normal general precipitation). For the best elastic spring properties for the 4 numbers hard material, a precipitation treatment of 4 hours at 200 degrees Cent. (390 degrees Fahr.) is indicated while a treatment of 4 hours at 250 degrees Cent. (480 degrees Fahr.) promises the best endurance properties. The best properties for the 8 numbers hard material appear to be developed by a treatment of 4 hours at 200 degrees Cent. (390 degrees Fahr.).

Similar observations are apparent from the data in Table 6 for the 65-35 brass 4 numbers and 8 numbers hard. The best combination of properties for the 4 numbers hard material appears to be developed by the precipitation treatment of 4 hours at 250 degrees Cent. (480 degrees Fahr.). The best properties for the 8 numbers hard appear to result from the precipitation treatment of 4 hours at 200 degrees Cent. (390 degrees Fahr.). A doubling of the pro-

Table II
Effect of Aging on Physical Properties

85-15 Brass

Condition	Prop'l Limit	Elastic Limit	Tensile Strength	Elong. Per Cent	Elec. Cond'y Per Cent	Rockwell B
Cold-Rolled 4 Nos. Hard:						
As cold-rolled	26,300	45,000	69,900	6	34.6	76
Aged 10 hrs. 175° C.	39,500	45,000	70,500	4	35.4	80
Aged 4 hrs. 200° C.	38,300	"slip"*	71,750	5	35.5	79
Aged 4 hrs. 250° C.	33,000	47,500	76,000	9	35.6	77
Cold-Rolled 8 Nos. Hard:						
As cold-rolled	30,000	30,000	80,000	3	34.0	84
Aged 10 hrs. 175° C.	36,900	45,000	83,300	3.5	34.7	88
Aged 4 hrs. 200° C.	40,000	55,000	81,050	4.0	35.0	87
Aged 4 hrs. 250° C.	36,400	40,000	78,600	5.0	35.2	85

*"Slip" = negative drift. (?) Shortening of sample.

portional limit in this last instance checks the earlier observation by Moore and Beckinsale (6).

For the majority of the treatments, the elongations showed surprising increases in view of the degree and direction of change noted in the values for the other tensile properties. This seems to be anomalous for the normal general precipitation reaction. A reasonable explanation for this increase in elongation, together with the observed (and usually advantageous) anomalies in proportional and elastic limits, seems to be that of strain-domain precipitation within individual grains. The domains of strain-induced precipitation

would act to maintain or increase the proportional limits, elastic limits, and age hardness while the trans-grain paths of lower solute content, once the elastic limit is exceeded, result in lower-than-expected tensile strengths, lower work hardening during test, and the

Table III
Effect of Aging on Physical Properties

65-35 Brass

Condition	Prop'l Limit	Elastic Limit	Tensile Strength	Elong. Per Cent	Elec. Cond'y Per Cent	Rockwell B
Cold-Rolled 4 Nos. Hard:						
As cold-rolled	30,000	40,000	75,700	5.5	25.8	80
Aged 10 hrs. 175° C.	37,000	47,500	76,000	7.5	26.4	85
Aged 4 hrs. 200° C.	30,600	42,500	74,700	8.0	26.4	83
Aged 4 hrs. 250° C.	37,000	47,500	71,400	11.0	26.5	81
Cold-Rolled 8 Nos. Hard:						
As cold-rolled	28,000	30,000	93,500	2.0	24.6	88
Aged 10 hrs. 175° C.	47,000	55,000	93,200	2.0	25.7	94
Aged 4 hrs. 200° C.	53,100	"slip"*	91,500	1.7	25.7	92
Aged 4 hrs. 250° C.	35,000	50,000	78,000	11.0	26.2	84

*"Slip" = negative drift. (?) Shortening of sample.

unusual increase in ductility. Of course, the electrical conductivity should, and does, increase.

Effect of Strain and Subsequent Aging on the Endurance Limit

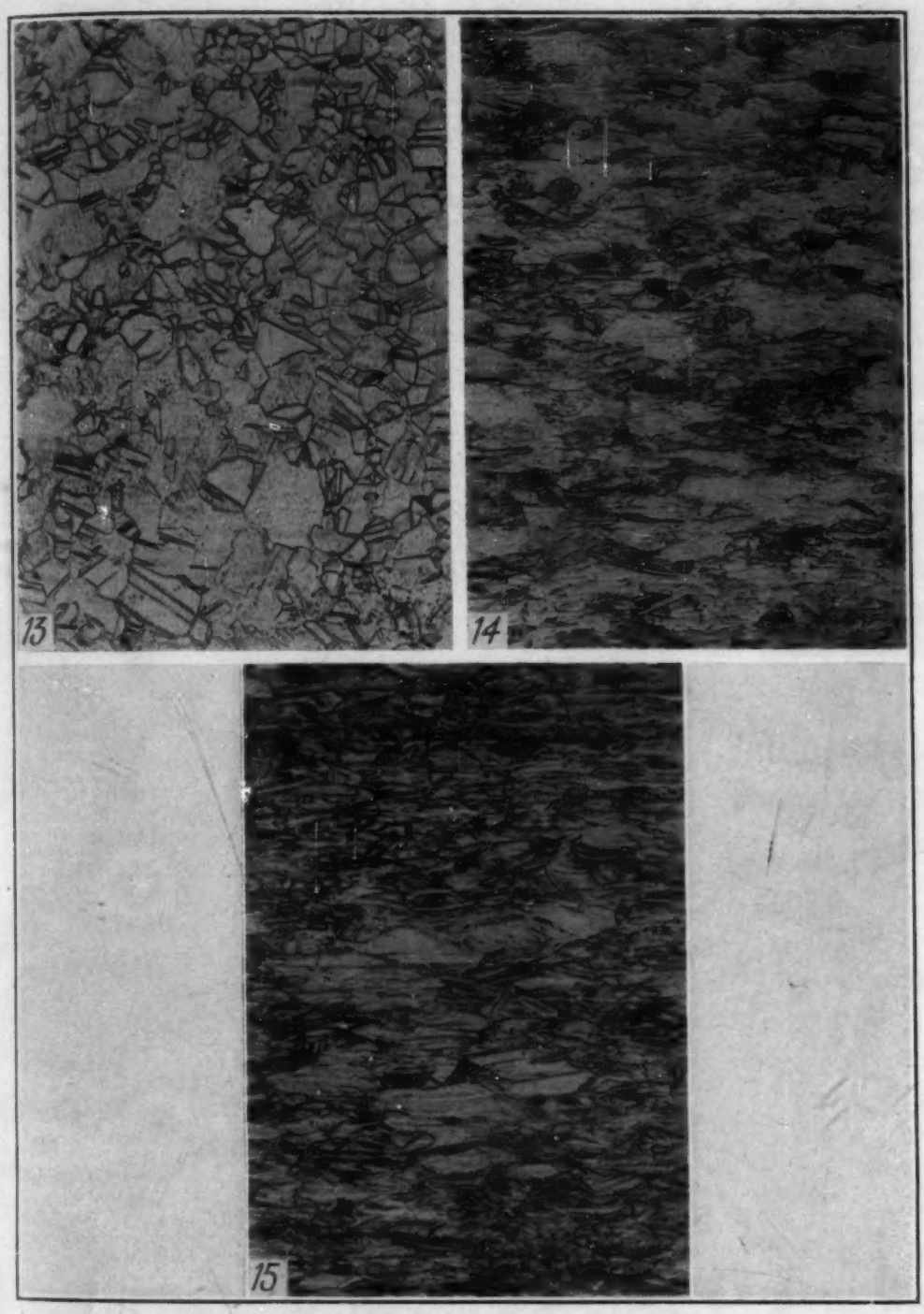
As in the case of aged, cold-rolled phosphor bronze (2), the induced precipitation reaction in these aged brasses apparently causes marked improvement in their fatigue properties. This effect of the aging treatment was independently and coincidentally discovered by R. J. Sutton* and his engineering associates, who have already made some very interesting engineering applications of the aged brasses. It is hoped that a report of this phase of the investigation will be forthcoming at an early date.

Photomicrographs

The appended photomicrographs, Figs. 13 through 24, show the structures for each of the four stock materials in the following three conditions:

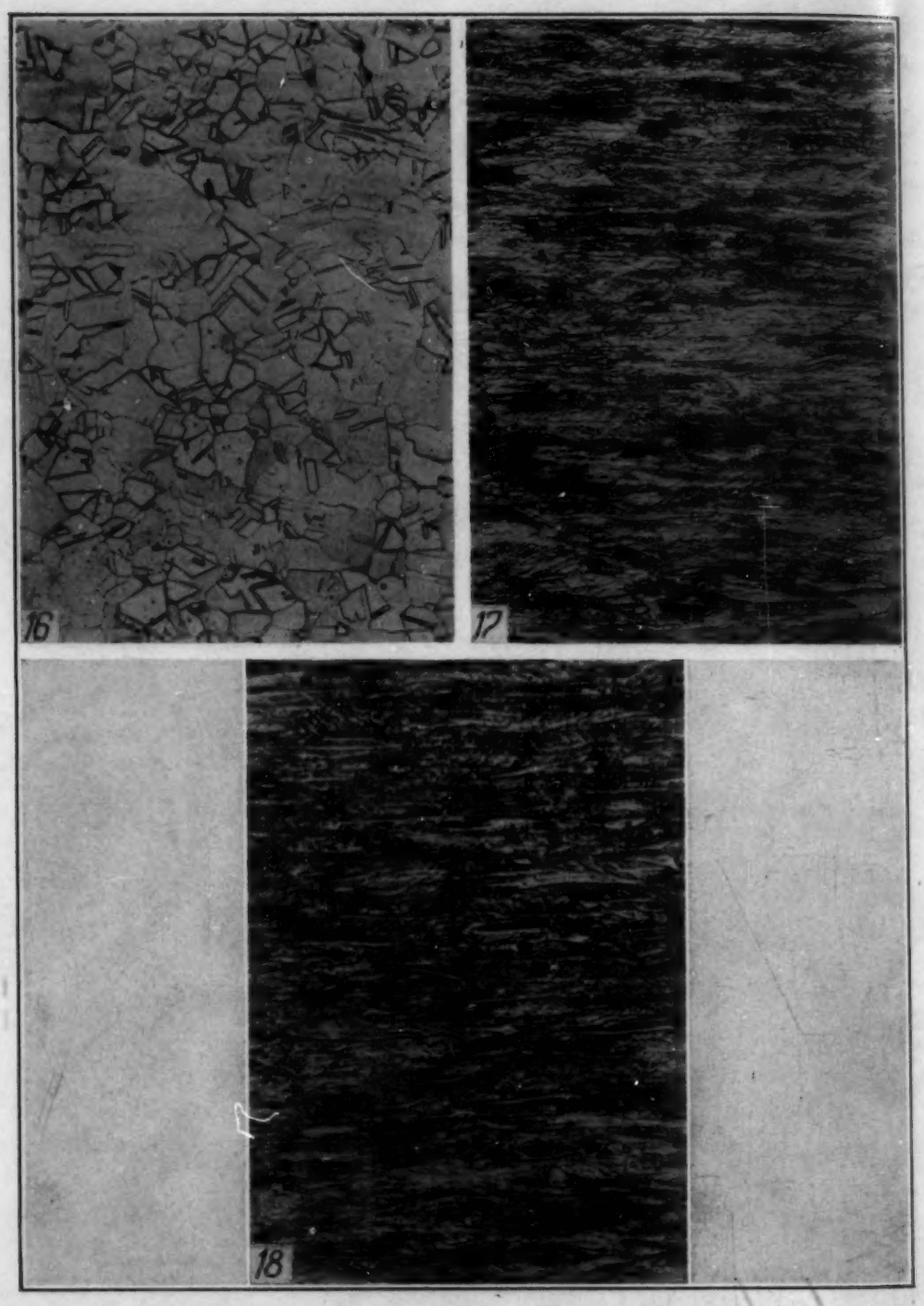
1. Commercially annealed previous to the final cold rolling.

*Engineer, Edison General Electric Company, Chicago.



Figs. 13 to 15—Structures of 85-15 Brass 4 Nos. Hard, When Subjected to the Following Treatments. Fig. 13—Annealed; Fig. 14—Cold-Rolled; Fig. 15—Aged 10 Hours at 175 Degrees Cent.

2. As cold-rolled (4 numbers or 8 numbers hard, as the case may be).



Figs. 16 to 18—Structures of 85-15 Brass 8 Nos. Hard, When Subjected to the Following Treatments. Fig. 16—Annealed; Fig. 17—Cold-Rolled; Fig. 18—Aged 10 Hours at 175 Degrees Cent.

3. The cold-rolled materials after subsequent aging for 10 hours at 175 degrees Cent. (345 degrees Fahr).

While the cold-rolled material shows sharply defined and focused structures, the corresponding aged material exhibits a cloudy, ill defined structure (as might be expected from submicroscopic precipitation-etching effects). All of the photomicrographs were taken at X100, and the etching re-agent was the standard mixture of $NH_4OH + H_2O_2$. Higher magnifications resulted in increasing loss of structure definition.

Conclusions

1. It seems well established that plastic strain induces a precipitation reaction in brasses at elevated temperatures below the recrystallization range (as previously reported for the phosphor bronzes).

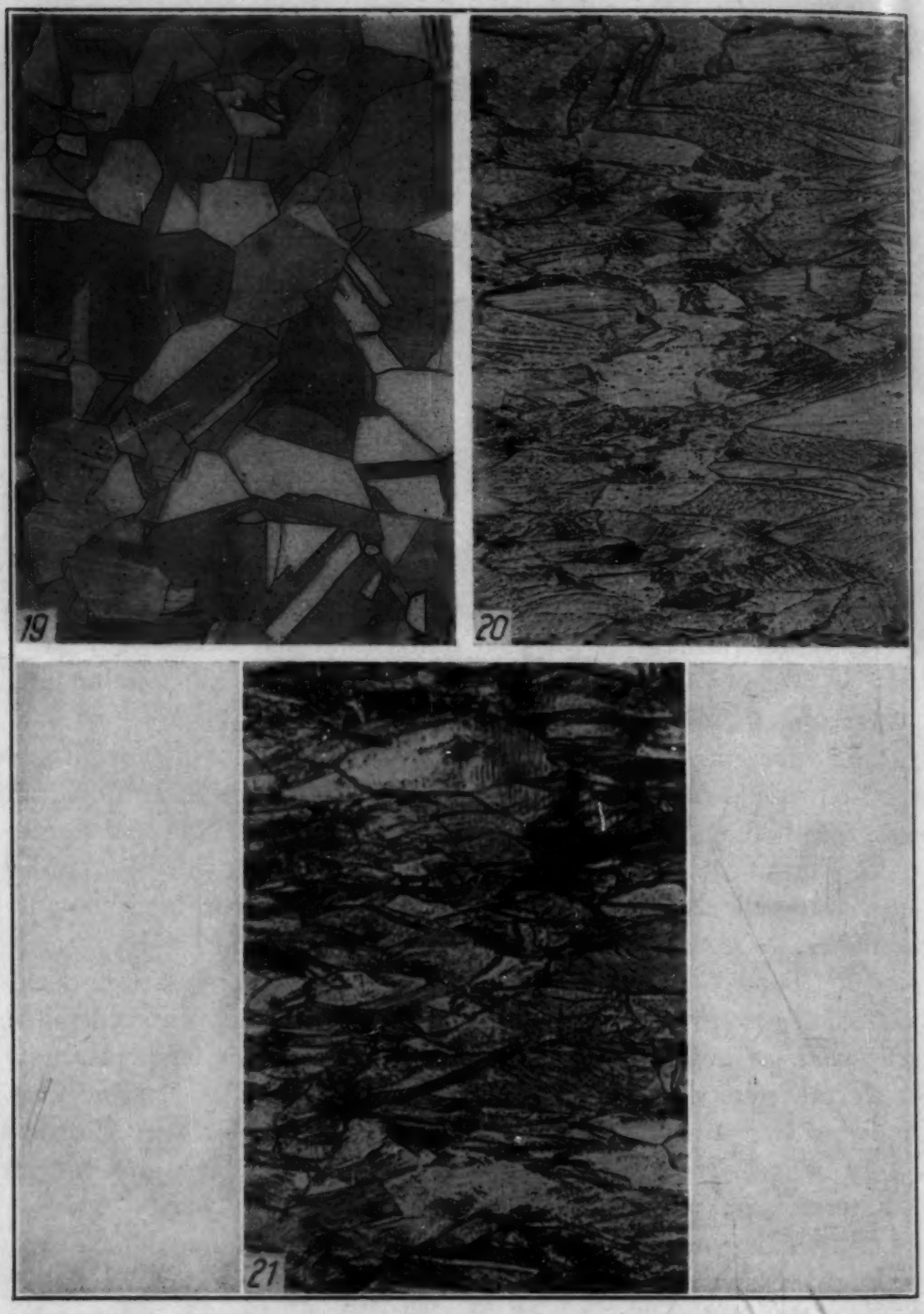
2. The induced precipitated phase acts as a blocking agent to the diffusion necessary for recrystallization. This results in higher service temperatures for the cold-rolled condition than would otherwise be obtained if the material were free to recrystallize unhindered at the lower temperatures.

3. Present data seem to indicate that this induced precipitation reaction should not be indicated on the standard equilibrium diagram but could perhaps be plotted in a plane parallel to the standard equilibrium diagram, displaced from the standard along a third (a strain) axis, perpendicular to the junction of the temperature and composition axes.

4. Controlled use of the induced precipitation reaction yields marked improvement in the engineering properties of the cold-rolled, solid-solution brasses, whether for service at room temperature or at elevated temperatures (up to 175 degrees Cent.). Specific practical heat treatments have been derived. The proportional and elastic limits may be increased from 30 to 90 per cent and resistance to fatigue is improved to a marked degree.

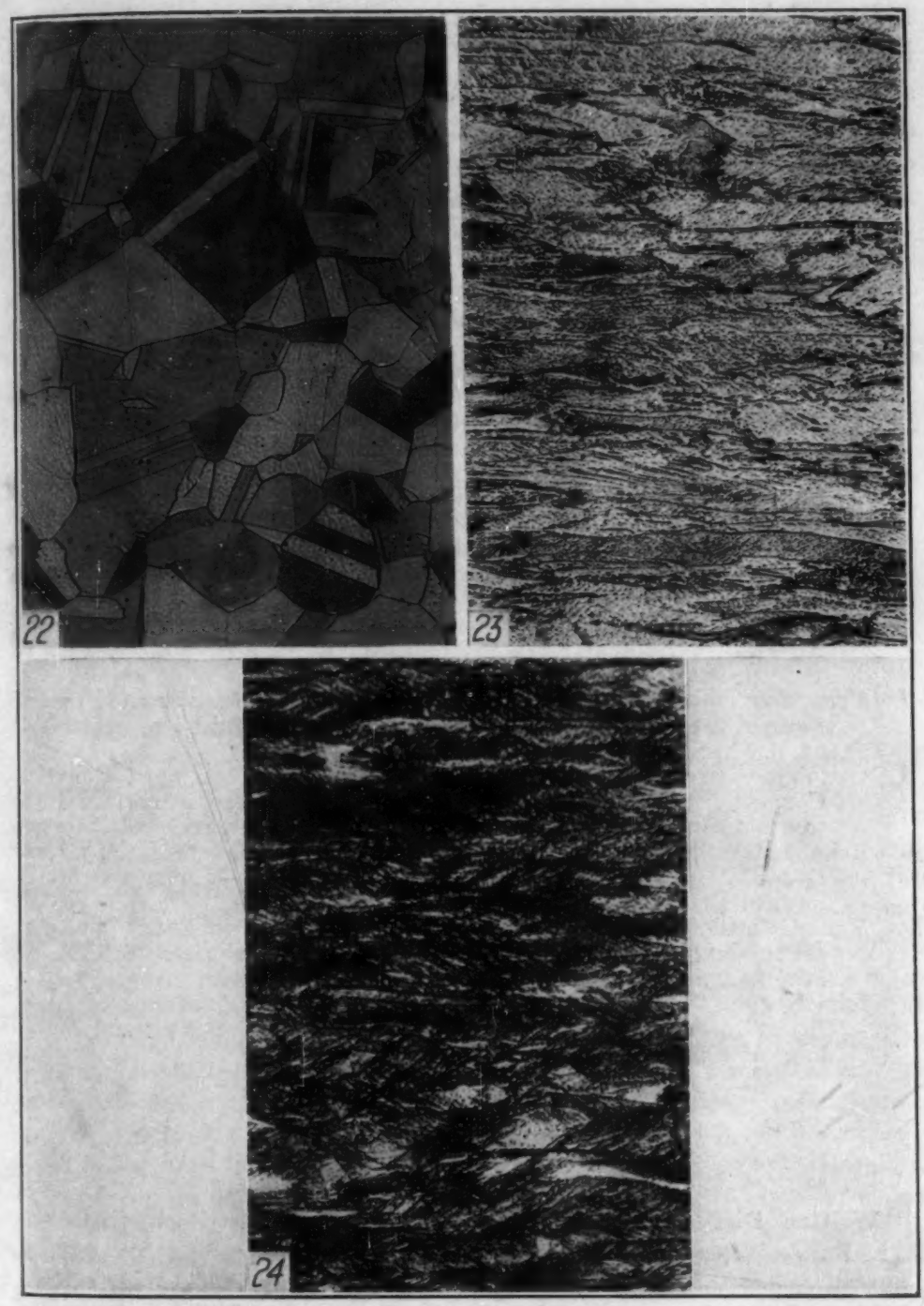
5. It is suggested that certain previously anomalous effects result from strain-domain precipitation within the grains of the initially cold-rolled material. (In the case of the brasses it is not impossible that this "precipitation" may involve a localized order-disorder reaction for copper-zinc as suggested in some of the references.)

6. Together with additional evidence (2), it is suggested that



Figs. 19 to 21—Structures of 65-35 Brass 4 Nos. Hard, When Subjected to the Following Treatments. Fig. 19—Annealed; Fig. 20—Cold-Rolled; Fig. 21—Aged 10 Hours at 175 Degrees Cent.

the principles and effects of this strain-induced precipitation should apply in some degree to all strained solid solution alloys.



Figs. 22 to 24—Structures of 65-35 Brass 8 Nos. Hard, When Subjected to the Following Treatments. Fig. 22—Annealed; Fig. 23—Cold-Rolled; Fig. 24—Aged 10 Hours at 175 Degrees Cent.

Acknowledgments

Appreciation is here expressed to the Stamford Rolling Mills

for supplying the sample material; to R. G. Thompson and O. C. Rutledge for the tensile tests; to S. S. Stack for the electrical resistance (conductivity) measurements; and to W. B. Conant for the photomicrographs (all the latter of the General Electric Company's laboratories).

Bibliography

1. R. H. Harrington, "The Role of Strain in Precipitation Reactions in Alloys," Age Hardening of Metals, published by American Society for Metals, 1940.
2. R. H. Harrington and R. G. Thompson, "The Precipitation Reaction in Cold-Rolled Phosphor Bronze," TRANSACTIONS, American Society for Metals, Vol. 28, 1940, p. 933-949.
3. Jeffries and Archer, "The Science of Metals, p. 189-191.
4. Bassett and Davis, "Comparison of Grain Size Measurements," *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 60, 1919, p. 428.
5. Mathewson and Phillips, "Recrystallization of Cold-Worked Alpha Brass on Annealing," *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 54, 1916, p. 611.
6. Moore and Beckinsale, "Prevention of Season Cracking in Brass by the Removal of Internal Stress," *Transactions,* Faraday Society, Vol. 17, 1921, p. 162.
7. Price and Davidson, "Physical Tests on Sheet Nickel-Silver," *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 64, p. 510-523.
8. Cramption, Berghoff and Stacy, "Effect of Cold Work upon Electrical Conductivity of Copper Alloys," *Metals Technology,* American Institute of Mining and Metallurgical Engineers, February, 1941.
9. Brick and Williamson, "Deformation and Recrystallization of Copper and Brass," *Metals Technology,* American Institute of Mining and Metallurgical Engineers, February, 1941.
10. Madigan and Blank, "Recovery and Recrystallization in Long Time Annealing of 70-30 Brass," *Metals Technology,* American Institute of Mining and Metallurgical Engineers, February, 1940.
11. John Norton, "Changes in Damping Capacity During Annealing of Alpha Brass," *Metals Technology,* American Institute of Mining and Metallurgical Engineers, February, 1940.

DISCUSSION

Written Discussion: By S. E. Maddigan, research physicist, and H. L. Burghoff, research metallurgist, Chase Brass & Copper Co., Waterbury, Conn.

The authors offer a new explanation for phenomena which have long been recognized as resulting from the low temperature annealing of brasses. These have previously been associated with the relief of internal stresses caused by the cold working. The improvement in elastic properties has been well known as have the changes in hardness, strength, electrical conductivity, and to a certain extent fatigue resistance.

The authors have not made any definite statement concerning the possible nature of their precipitated phase. As one ordinarily uses the term precipitation this phase should be different from that of the matrix; e.g., a precipitate of beta in the alpha matrix or, as an extreme use of the word, a formation of regions of local ordering. Perhaps the term might also be loosely applied to a recrystallization process where in the first stages the nuclei were of the same phase as the matrix but differing somewhat in composition. This latter might conceivably be the case for very small new particles where the surface energy and the strain energy terms become important in the total free energy expression and would tend to produce a shift in composition. This is adequately described under the term recrystallization.

A decrease in the alpha solubility limit at low temperatures would be necessary for the precipitation type of hardening due to a beta phase. Such a decrease would have to be far reaching to affect 85-15 brass or even 70-30 brass. Suggestions have been made in the literature that such a decrease in the solid solubility does occur to some extent. Conductivity changes observed by one of us[1] in low temperature anneals of 60-40 brass could be explained on this assumption although equally well by a shift in the alpha plus beta-beta boundary. However, any such change appeared to be small.

If the alpha solubility limit varies with pressure, then a precipitation might be expected at regions of stress concentration. Wilson[3] has investigated the alpha brasses under hydrostatic pressures up to 10,000 kilograms per square centimeter but found nothing to indicate any large shift in the solubility limit. This would seem to exclude a beta precipitate due to internal stresses.

The writers have previously suggested a reaction analogous to a precipitation effect due to formation of submicroscopic nuclei in the recrystallization process.[1, 2]

The photomicrographs presented here do not in any way clear up the question. The clouding observed is simply evidence of lack of resolution. Any submicroscopic particles differing from the matrix in etching characteristics, whether due to composition or to stress, would cause a similar clouding effect. Thus this phenomenon could be due either to recrystallization nucleation or to precipitation as ordinarily considered.

The conductivity changes can also be explained without recourse to a precipitation mechanism. According to the quantum mechanical interpretation, maximum conductivity requires a continuous, uniformly spaced lattice. Any disturbance of this condition, whether due to alloying, strain inhomogeneities, or boundary type of distortion, will cause a decrease in conductivity. This decrease is particularly great when the lattice variations have a spacing of 10 to 100 Å.[4] The X-ray investigations of Wood[5] have shown that fragmentation due to working has a lower limit of about 10^{-5} centimeters. This particle size remains apparently unchanged during short time low temperature

[1]D. K. Crampton, H. L. Burghoff, and J. T. Stacy, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 143, 1941, p. 228.

[2]S. E. Maddigan and A. I. Blank, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 137, 1940, p. 170.

[3]T. C. Wilson, *Physical Review*, Vol. 56, 1939, p. 598.

[4]J. Bardeen, *Journal Applied Physics*, Vol. 11, 1940, p. 88.

[5]W. A. Wood, *Proceedings*, Physical Society, Vol. 52, 1940, p. 110.

anneals. However, as suggested by the work of Boas[6] and many others, it is reasonable to believe that inhomogeneities exist within each crystallite fragment. These should then be within the range 10 to 100 Å. Due to their relatively short range, readjustment should occur in these short stress patterns before any other changes take place in the metal. As suggested by one of us, this readjustment probably occurs during the relief annealing treatment and can explain the large conductivity increases found in this stage.[2]

The anomalous increase in hardness, while a strong support for a precipitation reaction, can also be explained in another manner. A tentative explanation has already been offered by one of the writers on the basis of incipient nuclei. It is well recognized that a decrease in grain size causes an increase in hardness due to a slip interference at boundaries between grains of differing orientations.[7] The formation of large numbers of incipient nuclei by a similar boundary effect would tend to prevent free migration of dislocations through the matrix and would thus tend to increase the hardness. Such large numbers of nuclei of submicroscopic size are actually present in the range of anomalous hardness as shown by the fact that the hardness starts to decrease just at the time when recrystallization first becomes visible.[2] In the writers' work tensile strength and conductivity were studied for brasses annealed at temperatures from 100 degrees Cent. up to above the point of complete recrystallization.[1] Tensile strengths in the low temperature ranges showed a hardening process superimposed upon a normal recovery or softening effect, while conductivity values increased as the heating temperatures increased.

In this connection, it should be remembered that there is a corresponding decrease in conductivity when the materials are cold-worked, the magnitude of the effect being directly related to the degree of cold working. It might be thought, at first glance, that an improvement in conductivity in low temperature heat treatment can clearly be rationalized as a result of precipitation, but it is difficult to conceive that the cold working operation, which brought about the original decrease in conductivity, amounts to a solution treatment.

We would like to ask the authors whether their theoretical probability curves as in Fig. 1 have been corrected for the fact that the Rockwell-tensile strength curves are not linear but increase at a decreasing rate in the higher ranges. This would tend to throw the theoretical curve into better agreement with the experimental points. Analyses of the alloys used should be included.

Author's Reply

The authors welcome the discussion of Messrs. Maddigan and Burghoff and are particularly pleased to note that the discussers, while presenting the previously suggested theory of stress relief and nucleation for recrystallization, also point out that all of the data appear to completely support the theory of induced precipitation. Several interesting points of discussion have been raised:

1. The authors have not made any definite statement concerning the possible nature of their precipitated phase. The prime purpose of the present paper on the brasses and the preceding one on phosphor-bronze (and others to appear in the future) is simply to identify, if possible, the general type of

[6]List of references, G. W. Brindley, *Proceedings*, Physical Society, Vol. 52, 1940, p. 126.
[7]B. Chalmers, *Proceedings*, Physical Society, Vol. 52, 1940, p. 127.

reaction involved in aging all cold-worked solid solutions and to suggest the controlled use of that reaction for practical engineering applications. Some "pure research" aspects must await a less troubled future.

2. While the present paper deals chiefly with commercial brasses, it also presents the theory of induced precipitation in a general manner, including the strongly supporting evidence presented in a previous report on phosphor-bronze. Adequate discussion must admit use of any pertinent data.

3. The authors do not intend, and the data for the brasses and bronzes do not support, the very loose definition of precipitation suggested by the discussers. Progressive discussion can be based only upon the common acceptance of concise definitions. Concise definition of "precipitation," as intended and used in the present paper, has been presented in previous papers by the senior author. (See discussion "Theory of Age Hardening," Mehl and Jetter, American Society for Metals Symposium on Age Hardening of Metals.)

4. The discussers imply that such a "far-reaching" shift in solid solubility as would be necessary is practically impossible, even for a 70-30 brass. A decrease in solubility from about 40 to 30 per cent zinc and even to 15 per cent zinc is not at all impossible, as witness the orthodox temperature-composition diagram for the aluminum-zinc system. It must also be remembered, as pointed out in the authors' report on brass and the previous report on phosphor-bronze also by Dahl and Haase for tin-bronzes, U. S. Patent 2,128,122, that the degree of the effect depends upon the alloy system involved, the amount of solute element available, the rate of diffusion under internal stress, the amount of stress, the temperature of aging, and the time at aging temperature. Dr. S. L. Hoyt, in an attempt to indicate the induced precipitation in the tin-bronzes on an orthodox "constant pressure" equilibrium diagram, shows a decrease in solid solubility of tin in copper from 16 per cent tin to 2 per cent. This percentage decrease in solid solubility is much more than that required for induced precipitation in an 85-15 brass.

5. The discussers refer to the work of Wilson who has investigated 75-25 alpha brass under hydrostatic pressures and state that Wilson found nothing to indicate any large shift in the solubility limit and that this would seem to exclude a beta precipitate due to internal stress. This seems to be something of an error. Wilson was able to make only a limited study based on resistivity measurements of a ribbon heated through a temperature range. The strained material apparently was not heated for any length of time at constant temperature in the ranges of induced precipitation; and, under the experimental conditions, it seems probable that no plastic deformation could be effected. Yet Wilson reports a very real change occurred: "In going from 40 to 400 degrees Cent. (105 to 750 degrees Fahr.), there is an increase in the absolute magnitude of the pressure coefficient (of resistance) of alpha brass which is about one-third the increase in beta brass for the same temperature range. The relative increase is, however, somewhat greater than that of beta brass. If the interpretation which has been attached throughout this analysis (except for alpha brass, dealing with specific compositions yielding only order-disorder reactions) to an increase with temperature of the pressure coefficient of resistance is correct, the conclusion must be drawn that an ordered phase in alpha brass is promoted by pressure." In view of the authors' report

on brass and the previous report on bronze, it seems quite probable that Wilson actually measured the effect of the early nucleation stage of the precipitation reaction induced in the alpha brass under hydrostatic pressure.

6. The discussers present in detail an alternative theory of recrystallization-nucleation overlapping stress relief to account for all of the measured property changes. The authors believe that this is an unwieldy theory at best and cannot reconcile the use of this theory in accounting for both an increase in hardness and a coincident increase in elongation. Furthermore, the discussers' theory, plus any quantum mechanical interpretation involved, cannot account for an electrical conductivity in the aged material, 17 per cent greater than that of the fully annealed material, as reported for phosphor-bronze by the senior author. (Dahl and Haase report as much as 40 per cent increase in electrical conductivity for 90 per cent cold-rolled tin-bronze, aged for 1000 hours at 175 to 200 degrees Cent. (340 to 390 degrees Fahr.); that is, an electrical conductivity 40 per cent in excess of that for fully annealed tin-bronze.) Any suitable theory must apply to all measured effects for the same reaction occurring in all alloys of the same class.

7. The authors placed no value on the photomicrographs presented in either the paper on brass or the one on bronze.

8. The discussers state "that it might be thought, at first glance, that an improvement in conductivity in low-temperature heat treatment can clearly be rationalized as a result of precipitation, but it is certainly difficult to conceive that the cold working operation, which brought about the original decrease in conductivity, amounts to a solution treatment." This statement, taken literally as phrased, does make the conception difficult, but the difficulty is purely artificial. In applying the phase rule to metallurgy, the original error came about in eliminating "pressure" as a variable from the viewpoint that all alloy material was under constant pressure, that of the atmosphere. Such is distinctly a grave error. For instance, in cold-worked solid solutions, there are multitudinous stress-gradient volumes, each of which reacts more or less as an individual system on low-temperature aging as long as it exists. The unabrogated phase rule definitely postulates the possibility of inducing the formation of a new phase under these conditions. In fact, it is only on this basis that the results found by Wilson as cited above can be explained.

9. The discussers have asked the authors "whether their theoretical probability curves (as in Fig. 1) have been corrected for the fact that the Rockwell tensile strength curves are not linear but increase at a decreasing rate in the higher ranges. This would tend to throw the theoretical curve into better agreement with the experimental points." The authors have presented no Rockwell tensile strength curves. The probability curves represent the assumed relationship of hardness to temperature for the recrystallization of cold-worked solid solutions were there no induced precipitation.

This discussion is a very difficult one to present in a brief and still concise written form. The authors do appreciate sincerely the discussion offered by Maddigan and Burghoff and, in conclusion, would like to suggest that the theory elucidated by the discussers is very valuable and would undoubtedly apply more simply and clearly to the recrystallization of a cold-worked pure metal, in the absence of any possibility of an induced precipitation reaction.

HARDENING CHARACTERISTICS OF AN IRON-COBALT-TUNGSTEN ALLOY

By W. P. Sykes

Abstract

This paper deals with the hardening performance of a ternary iron-cobalt-tungsten alloy. A comparison is drawn between the behavior of this alloy and that of binary iron-tungsten compositions of approximately equivalent tungsten concentrations.

The ternary alloy becomes progressively softer as the temperature of solution treatment is increased from 1100 to 1400 degrees Cent. (2010 to 2550 degrees Fahr.). From 1100 and 1200 degrees Cent. (2010 and 2190 degrees Fahr.), air cooling results in a greater hardness than does water quenching.

At an aging temperature of 400 degrees Cent. (750 degrees Fahr.), the hardness of the ternary alloy increases at a moderate rate, whereas the binary alloy requires a temperature of 575 degrees Cent. (1065 degrees Fahr.) to harden in a comparable manner. The precipitation hardening phenomenon in the case of the ternary alloy appears to lack the familiar "incubation period".

Temperature of solution treatment and resulting change in tungsten concentration of the solid solution has but slight effect upon the rate of hardening or the maximum hardness developed during aging. The higher solution temperatures and correspondingly higher tungsten concentrations result in greatest resistance to softening during prolonged aging at 600 and 700 degrees Cent. (1110 and 1290 degrees Fahr.). Some possible explanations for these observed differences are suggested.

Introduction

THE precipitation hardening performance of binary iron-tungsten alloys has been investigated and described recently in some detail (1).[1] This series represents the case of a solute metal of low

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. The author, W. P. Sykes, is metallurgical engineer, General Electric Co., Cleveland Wire Works, Cleveland. Manuscript received June 11, 1941.

diffusion rate in a solid solution which undergoes no allotropic transformation throughout a considerable range of temperatures and concentrations.

In the ternary iron-cobalt-tungsten system there exist iron-rich solid solutions which undergo the gamma to alpha allotropic change upon cooling from temperatures above 950 degrees Cent. (1740 degrees Fahr.). On account of the low diffusion rate of tungsten in iron, it is possible in such alloys to obtain at room temperature a structure consisting of alpha solid solution highly supersaturated with tungsten. Having been formed by the transformation of the gamma phase (an austenite practically carbon free), this ferrite or alpha solid solution of small grain size is analogous to the untempered martensite of the iron-carbon series.

An alloy of this sort responds to subsequent tempering or precipitation treatment in quite a different manner than does the binary iron-tungsten alloy of equivalent tungsten concentration. While this behavior has already been briefly described (2), (3), a more detailed investigation seemed warranted in view of the fundamental aspects of precipitation hardening phenomena. Furthermore, certain compositions in this ternary system have features in common with the steels and hence might be expected to yield information bearing on the nature of the hardening performance observed in both groups of alloys.

Composition and Preparation of Alloy

The composition chosen for this investigation, 50 per cent iron, 30 per cent cobalt and 20 per cent tungsten, lies in the ternary section shown in Fig. 1. It was melted from armco ingot iron, cobalt rondelles and high purity tungsten in the magnesia crucible of an induction furnace. Ingots, 1½ inches in diameter and 12 inches in length, were swaged to a finished diameter of ½ inch at temperatures of 1100 to 1200 degrees Cent. (2010 to 2190 degrees Fahr.). Partial analyses of the four heats prepared for this work appear below:

Tungsten		Cobalt
19.95 to 20.30 per cent		29.80 to 30.50 per cent
Silicon	Manganese	Carbon
0.09 to 0.12 per cent	0.15 to 0.20 per cent	0.03 to 0.05 per cent

Specimens for thermal treatment, about ⅜ inch in length, were cut

from swaged rods. Solution treatments were carried out for 30-minute periods in the hydrogen atmosphere of a tungsten wound resistor furnace, the specimens being subsequently cooled either in air or by quenching in water at 20 degrees Cent. (70 degrees Fahr.).

Structural Nature of the Alloy

As shown in Fig. 1, the structure of this alloy at a temperature of 1400 degrees Cent. (2550 degrees Fahr.) consists entirely

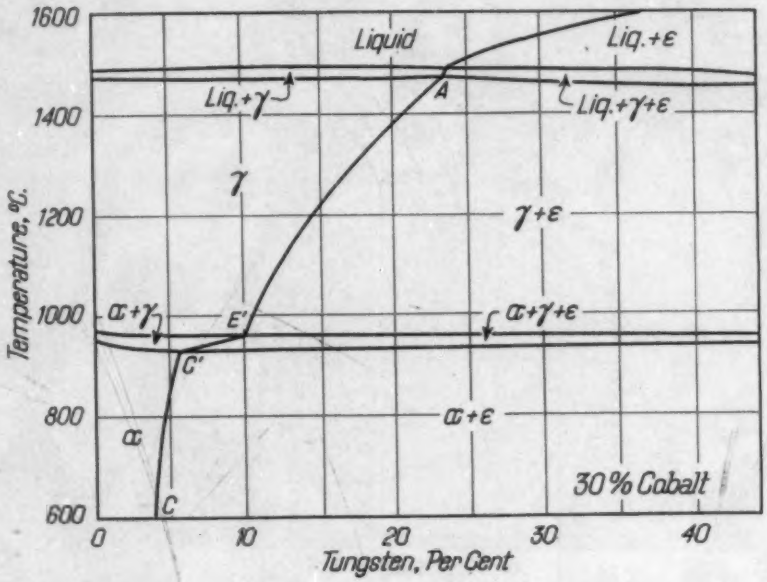


Fig. 1—Section Through Ternary System at 30 Per Cent Cobalt.

of a gamma solution or austenite. Under conditions of very slow cooling the tungsten content of the austenite decreases from 20 per cent to about 10 per cent at 950 degrees Cent. (1740 degrees Fahr.) by precipitation of the iron-cobalt-tungsten phase, epsilon. Upon further cooling through a range of some 30 or 40 degrees Cent. immediately below the point E′, the austenite decomposes into (a) alpha solid solution of composition C′, and (b) the epsilon phase. This reaction, $\gamma = \alpha + \varepsilon$, is analogous to the decomposition of iron-carbon austenite which results in the formation of pearlite. Indeed, the ternary alloy develops a similar structure as the result of gamma decomposition at temperatures somewhat below 950 degrees Cent. (1740 degrees Fahr.) (3).

Effect of Solution Temperature Upon Hardness in (A) Water-Quenched or (B) Air-Cooled Condition

As cooled to room temperature in water or in air from solution treatments at a series of temperatures, the hardness of the alloy varies as shown in Fig. 2. These values represent averages of several readings upon each of some fifty specimens treated as described. The

Table I

Maximum and Minimum Rockwell C Hardness of Ternary Alloy as Solution Treated

Temperature of Treatment			
Degrees Cent.	Degrees Fahr.	Air-Cooled	Water-Quenched
1100	2010	48–51	43–45
1200	2190	45–47	43–45
1300	2370	41–43	40–43
1400	2550	37–40	37–39

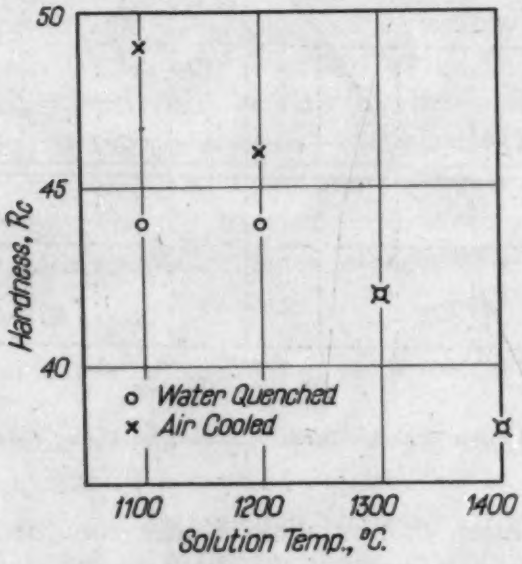


Fig. 2—Hardness of Ternary Alloy as Water-Quenched and as Air-Cooled from Various Temperatures.

treatments were carried out at intervals extending over a period of about one year and the maximum and minimum hardness values observed are listed in Table I.

The positive trend toward lower hardness with increasing solution temperatures is obvious in both the air-cooled and the water-quenched state. Air cooling from 1100 and 1200 degrees Cent. (2010 and 2190 degrees Fahr.), moreover, unquestionably results in higher hardness than does water quenching from these temperatures.

The softening effect of higher solution temperatures might be attributed to the following possibilities: (A) Decrease in amount of undissolved epsilon, a relatively hard phase, as shown by comparison of the structures in Figs. 3 and 4. (B) Increase in the quantity of retained austenite, due to the stabilizing effect of higher tungsten concentration and larger grain diameter. The available evidence bearing

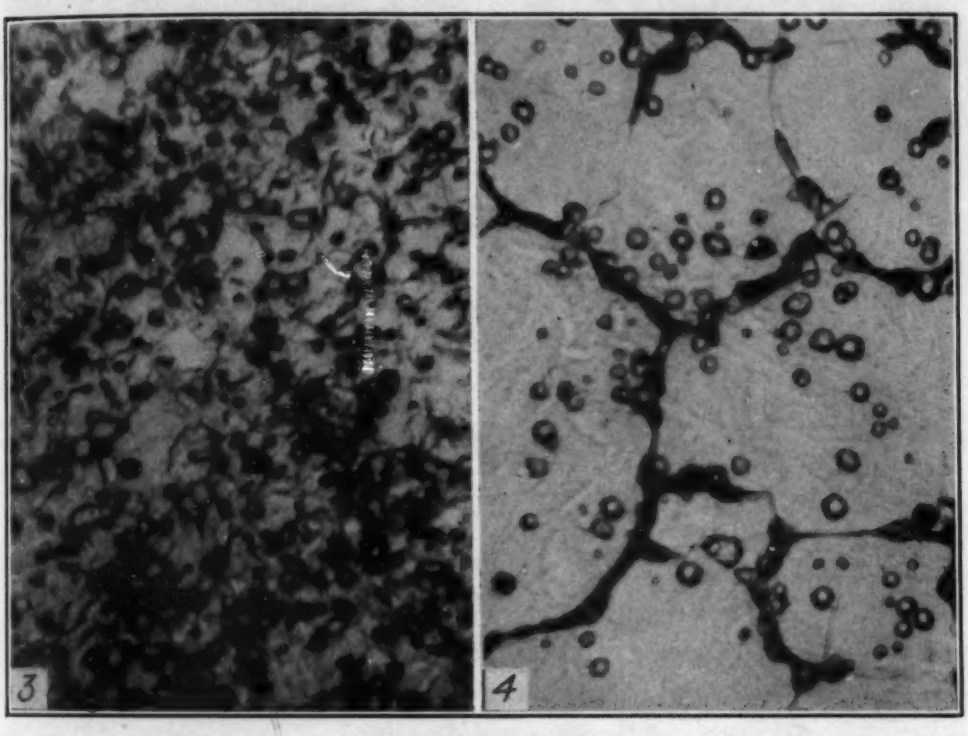


Fig. 3—Iron 50 Per Cent, Cobalt 30 Per Cent, Tungsten 20 Per Cent. Heated 30 Minutes at 1100 Degrees Cent. Water-Quenched. Etched 5 Seconds, 4 Parts H_2O_2; 1 Part H_3PO_4. Shows Undissolved Epsilon in Matrix of Alpha. × 2000.
Fig. 4—Ternary Alloy. Heated 30 Minutes at 1300 Degrees Cent. Air Cooled. × 2000.

upon austenite retention will be considered later, although it should be observed at this point that a water quench might be expected to further the gamma to alpha transformation.

The higher hardness of the alloy as cooled from 1100 and 1200 degrees Cent. (2010 and 2190 degrees Fahr.) at the lower rate may reasonably be attributed to an appreciable decomposition of austenite over a temperature range immediately below 950 degrees Cent. (1740 degrees Fahr.), i.e., the Ar′ range.

This reaction should be favored by (A) small diameter of austenite grain, (B) low tungsten concentration of the solid solution and (C) a large amount of residual epsilon. The darkly etched network visible in Fig. 5 may represent the beginning of gamma decomposi-

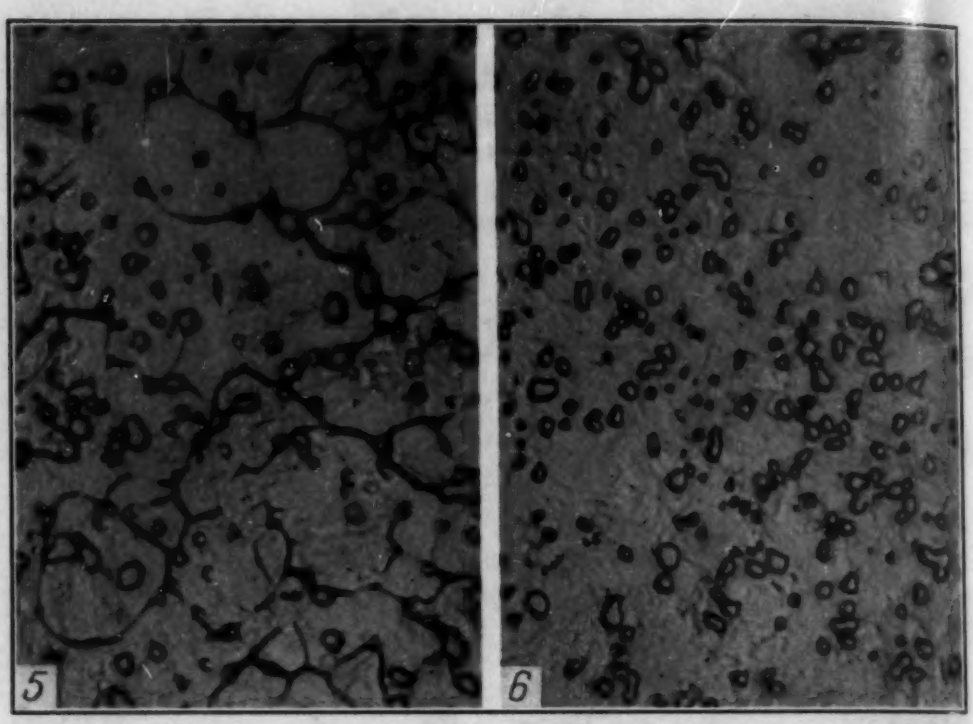


Fig. 5—Ternary Alloy. Heated 30 Minutes at 1200 Degrees Cent. Air-Cooled. Darkened Network Probably Result of Gamma Decomposition During Cooling. × 2000.
Fig. 6—Ternary Alloy. Heated 30 Minutes at 1200 Degrees Cent. Water-Quenched. × 2000.

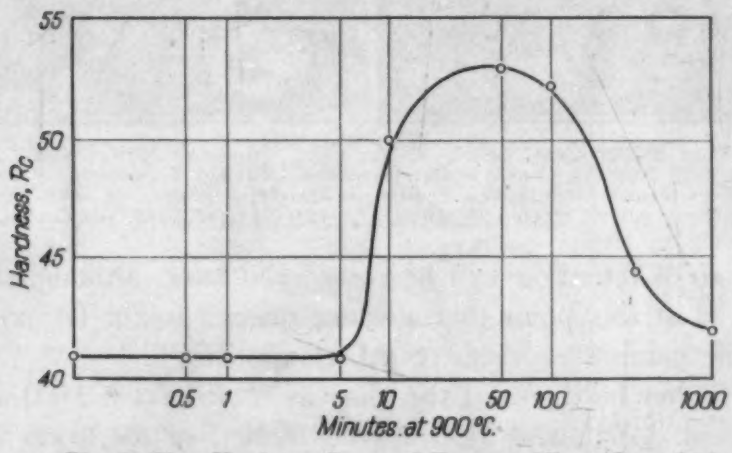


Fig. 7—Time-Hardness Curve of Ternary Alloy. Quenched from 1300 Degrees Cent. Into Lead at 900 Degrees Cent. Water-Quenched After Holding at 900 Degrees Cent. for Time Indicated.

tion since it does not appear in the water-quenched specimens as shown in Fig. 6.

The hardening which accompanies isothermal decomposition (austempering) of this alloy at 900 degrees Cent. (1650 degrees

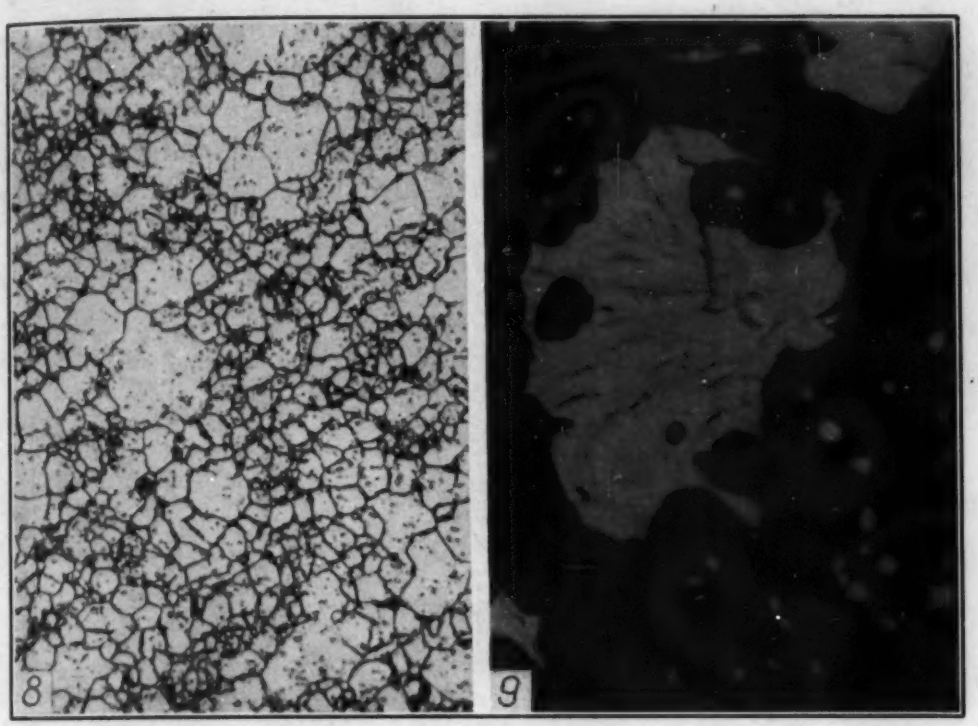


Fig. 8—Ternary Alloy. Quenched from 1300 Degrees Cent. Into Lead at 600 Degrees Cent. Held 5 Hours at 600 Degrees Cent. and Water-Quenched. × 200.
Fig. 9—Ternary Alloy. Quenched from 1300 Degrees Cent. Into Lead at 600 Degrees Cent. and Held 25 Hours Before Water Quenching. Lighter Portion Was Austenite Before Final Quench. Darker Portion Represents Alpha + Epsilon Formed by Decomposition of Gamma at 600 Degrees Cent. × 2000.

Fahr.) is illustrated by Fig. 7, while the structures characterizing the early and advanced stages of this reaction at 600 degrees Cent. (1110 degrees Fahr.) appear in Figs. 8 and 9.

Hardening by Precipitation Treatment After Cooling to Room Temperature

Precipitation treatments at 400, 500, 600 and 700 degrees Cent. (750, 930, 1110 and 1290 degrees Fahr.) were given the alloy as

Table II

Rockwell C Hardness of Ternary Alloy as Water-Quenched from 1300 Degrees Cent. (2370 Degrees Fahr.) and Aged at 300 Degrees Cent. (570 Degrees Fahr.)

Initial Hardness	Hours at 300 Degrees Cent. (570 Degrees Fahr.)						
	1	5	25	50	100	200	300
41–41	41–42	42–43	43–43	43–44	44–44	44–45	45–45

air-cooled and as water-quenched from the four solution temperatures. One pair of specimens was heated successively for the shorter

periods totaling 25 hours. A second pair served for the intervals between 25 and 300 or 400 hours. The data in the accompanying time-hardness curves thus represent two sets of multiple treatments overlapping at the 25-hour period. Since the maximum variation in initial hardness of specimens treated together seldom exceeded plus

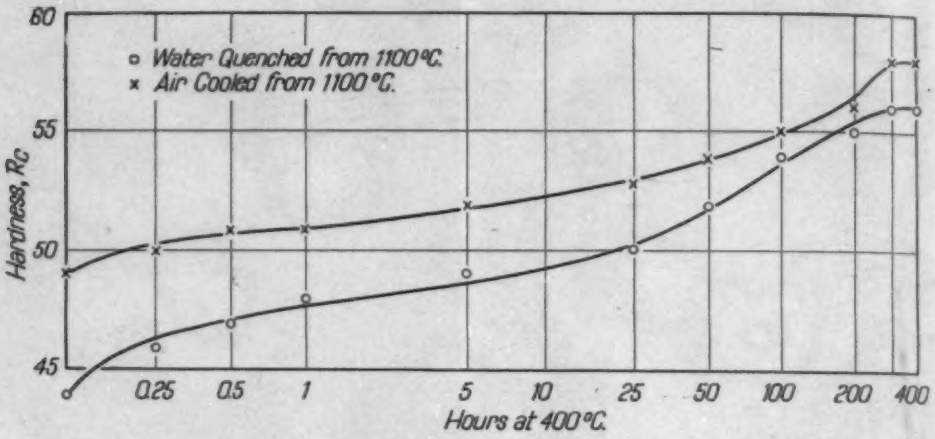


Fig. 10—Time-Hardness Curves of Ternary Alloy Aged at 400 Degrees Cent.

or minus one half unit, readings were recorded to the nearest unit. This variation became less as hardening progressed.

When aged at 300 degrees Cent. (570 degrees Fahr.) the ternary alloy exhibits a small but measurable rise in hardness, extending over the 300-hour period of treatment, as may be observed by reference to Table II.

The hardness increases at an appreciable rate during aging at temperatures as low as 400 degrees Cent. (750 degrees Fahr.). This is shown in Fig. 10 which serves also to compare the performances of the air-cooled and the water-quenched specimens. At this temperature of aging, the alloy as air-cooled from 1100 degrees Cent. (2010 degrees Fahr.) remains the harder over a period of 400 hours. This effect of cooling rate from solution treatment vanishes as the solution temperatures rises to 1200 degrees Cent. (2190 degrees Fahr.), as shown by the time-hardness data in Table III. Consequently one curve serves for both cooling rates when the solution treatment has been carried out at a temperature of 1200 degrees Cent. (2190 degrees Fahr.) or higher.

In Figs. 11 and 12 the hardening performance may be observed as influenced by the solution temperature. The noteworthy features of these curves would appear to be (a) the immediate hardness rise

Table III

Rockwell C Hardness of Ternary Alloy as (a) Air-Cooled and (b) Water-Quenched from 1200 Degrees Cent. (2190 Degrees Fahr.) and Aged at 400 Degrees Cent. (750 Degrees Fahr.)

Specimen (Pairs)	As Air-Cooled	As Water-Quenched	Hours at 400 Degrees Cent. (750 Degrees Fahr.) 0.25	0.50	1	5	25	50	100	200	300	400
0	45–46	...	47–47	47–48	48–49	49–49	52–53	...	...	...	...	...
1	46–46	...	...	...	...	...	52–53	53–54	55–55	56–56	57–57	57–58
2	...	44–45	47–48	48–48	48–49	49–50	53–53	...	...	...	...	...
3	...	45–45	...	...	...	...	52–53	54–54	55–55	56–57	57–58	58–59

which occurs during the first 15-minute aging period, and (b) the relative hardness values, both initial and final (after 400 hours).

As the temperature of precipitation treatment is raised to 500 degrees Cent. (930 degrees Fahr.) the specimens both as quenched

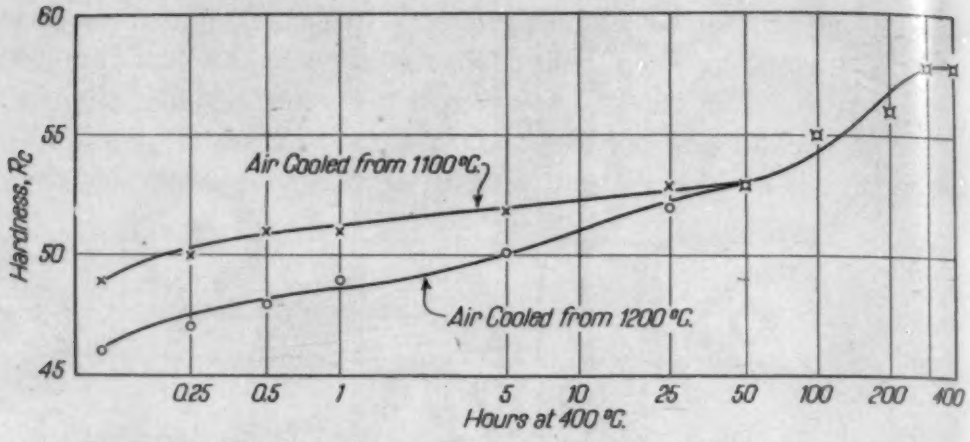


Fig. 11—Time-Hardness Curves of Ternary Alloy Aged at 400 Degrees Cent.

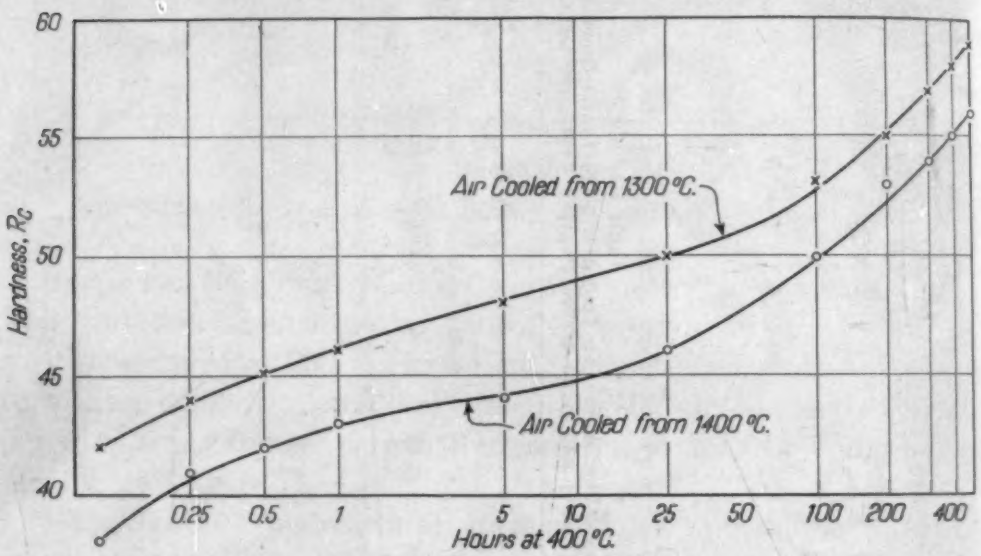


Fig. 12—Time-Hardness Curves of Ternary Alloy Aged at 400 Degrees Cent.

and as air-cooled from 1100 degrees Cent. (2010 degrees Fahr.) develop the same hardness within a period of 5 hours. No measurable difference between the two is observed thereafter while the treatment in continued through 200 hours as shown in Fig. 13.

In Fig. 14 are shown the hardening curves of the alloy as air-cooled from each of the four solution temperatures and subsequently aged at 500 degrees Cent. (930 degrees Fahr.). To simplify the figure, one curve only is drawn complete.

Here again the immediate hardness rise is evident in every case. The specimens solution treated at 1100, 1200 and 1300 degrees Cent. (2010, 2190 and 2370 degrees Fahr.) diverge but slightly from a common course, although the 1300 degrees Cent. (2370 degrees Fahr.)

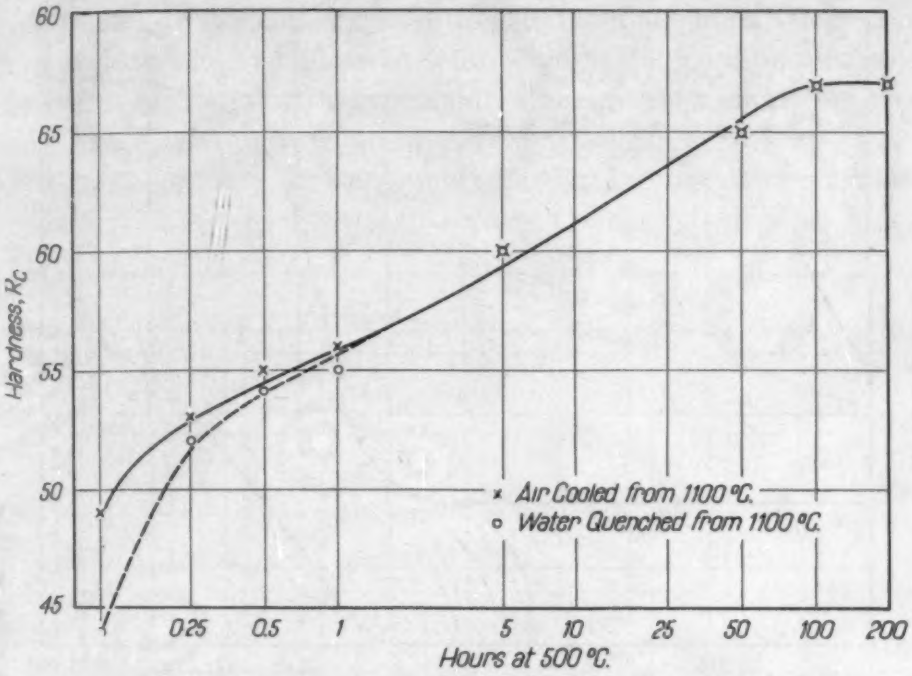


Fig. 13—Time-Hardness Curves of Ternary Alloy Aged at 500 Degrees Cent.

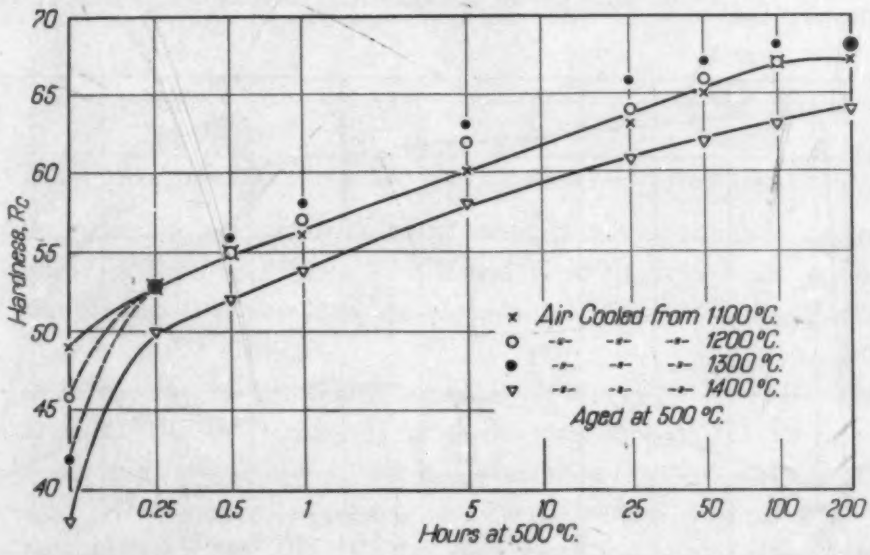


Fig. 14—Time-Hardness Curves of Ternary Alloy Aged at 500 Degrees Cent.

treatment appears to develop the maximum hardness first of all after 100 hours. At the end of 200 hours this value is equalled by that of the 1200 degrees Cent. (2190 degrees Fahr.) treatment. Throughout the 200-hour period the 1400 degrees Cent. (2550 degrees Fahr.) specimen is the softest of the series, although it has shown a continuous hardness increase.

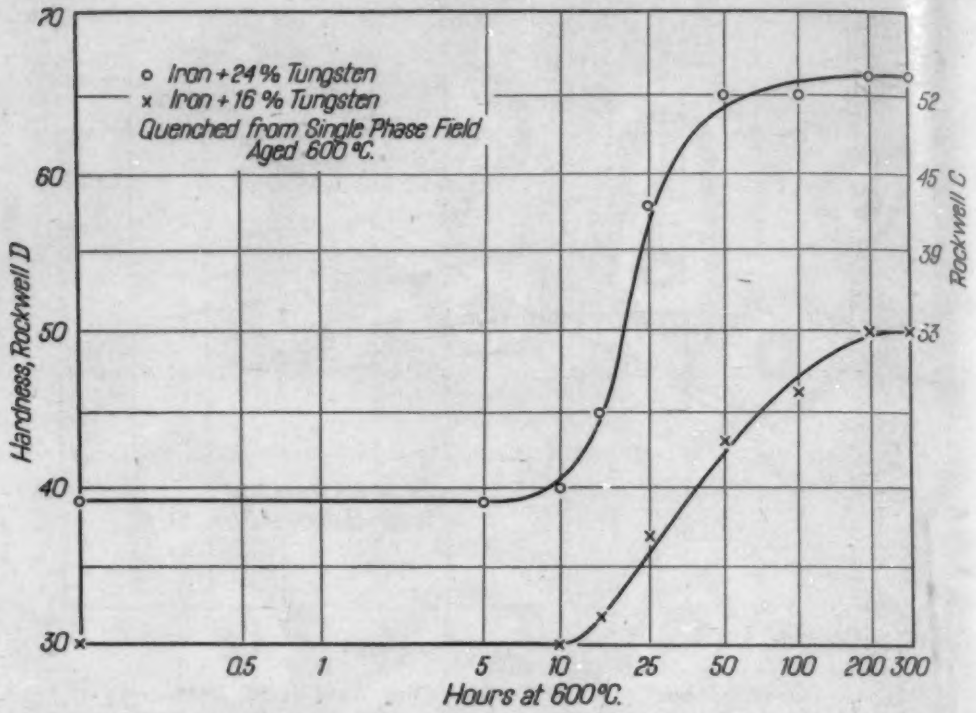


Fig. 15—Time-Hardness Curves of Binary Iron-Tungsten Alloys Aged at 600 Degrees Cent.

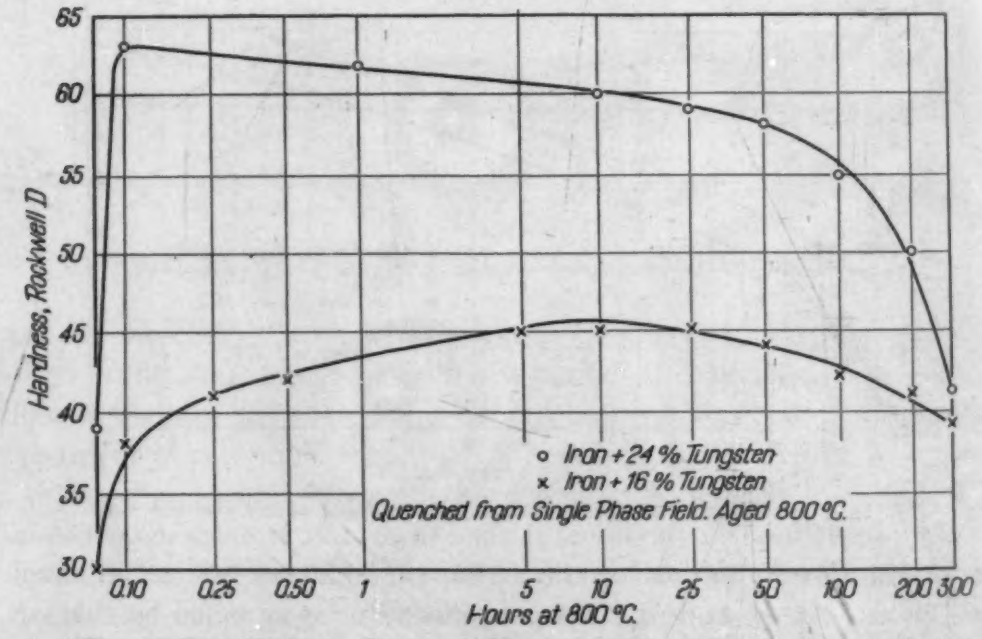


Fig. 16—Time-Hardness Curves of Binary Iron-Tungsten Alloys Aged at 800 Degrees Cent.

The alloy as treated at 1400 degrees Cent. (2550 degrees Fahr.) represents the solid solution of highest tungsten concentration. Pre-

vious studies of the binary iron-tungsten compositions have shown that with increasing tungsten in solid solution the maximum hardness rises and is also attained more rapidly during the precipitation treatment. These relationships are apparent from the curves in Figs. 15 and 16, and certainly find no counterpart in the behavior of the ternary alloy during aging at 500 degrees Cent. (930 degrees Fahr.).

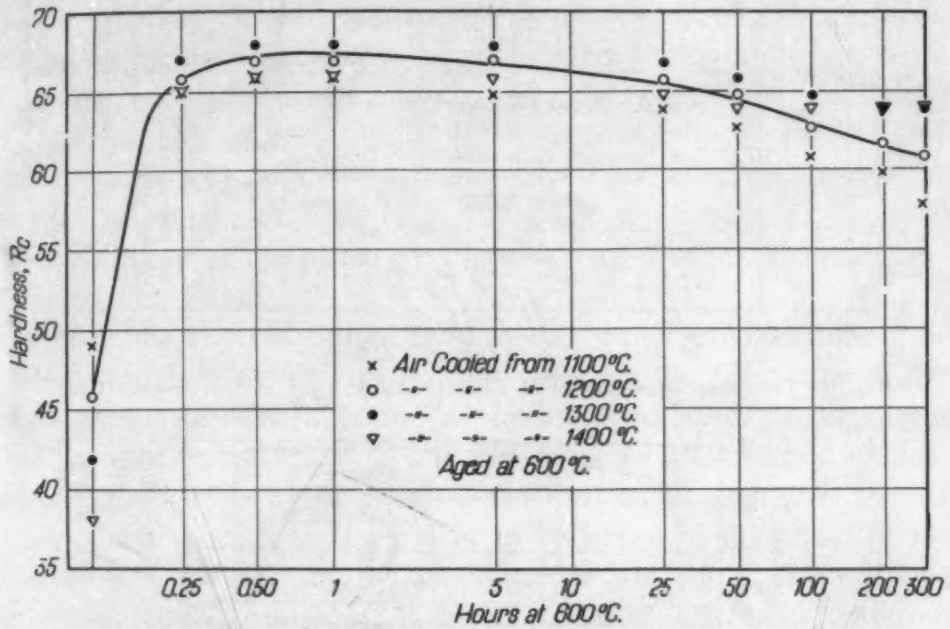


Fig. 17—Time-Hardness Curves of Ternary Alloy Aged at 600 Degrees Cent.

However, as the temperature of precipitation treatment is increased to 600 and 700 degrees Cent. (1110 and 1290 degrees Fahr.), a similar relationship between tungsten concentration and hardening performance becomes evident.

A precipitation treatment at 600 degrees Cent. (1110 degrees Fahr.) results in the hardness changes shown in Fig. 17. In this case all the maxima are attained within a period of 1 hour and are nearly identical. With continued aging, however, the less concentrated solid solutions soften more rapidly than do those treated at 1300 and 1400 degrees Cent. (2370 and 2550 degrees Fahr.). The latter two exhibit no decrease in hardness over the final 100-hour interval.

This resistance to overaging imparted to the alloy by the higher solution temperatures is even more apparent in Fig. 18, which illustrates the hardening performance at 700 degrees Cent. (1290 degrees Fahr.). Here all the hardness maxima appear at the end of the initial 15-minute period. The highest of these values is shared by those

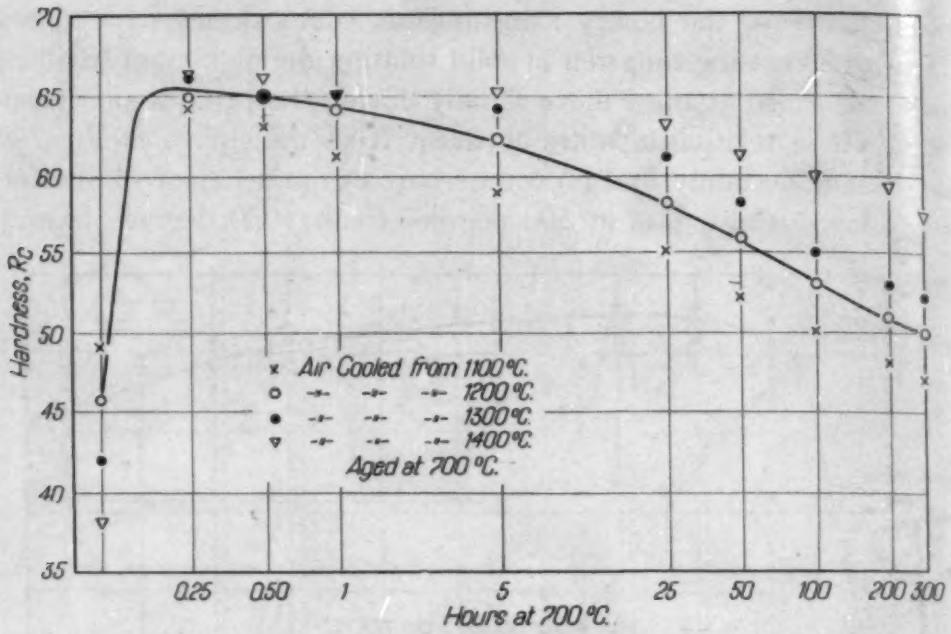


Fig. 18—Time-Hardness Curves of Ternary Alloy Aged at 700 Degrees Cent.

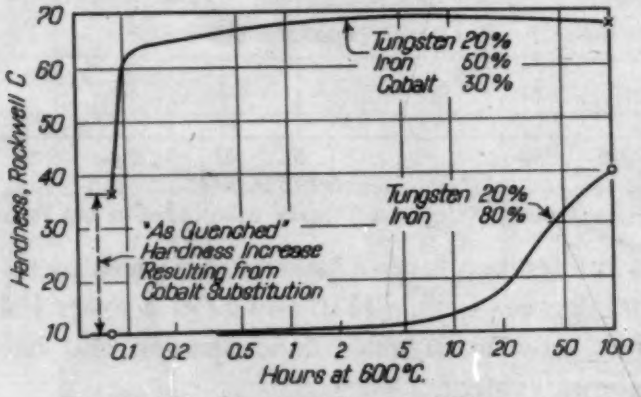


Fig. 19—Time-Hardness Curves of Binary and Ternary Alloys Aged at 600 Degrees Cent.

specimens solution treated at 1300 and 1400 degrees Cent. (2370 and 2550 degrees Fahr.). This quality persists throughout an interval of 5 hours, when the superior stability of the higher tungsten concentration becomes evident. After 300 hours the hardness values have assumed an order increasing with the temperature of their respective solution treatments.

Discussion of Foregoing Data

The characteristics marking the hardening performance in the ternary alloy under consideration may perhaps be best emphasized

by comparison with the iron-tungsten solid solutions of similar tungsten content.

As may be observed in Fig. 19, the ternary alloy as solution treated at 1300 degrees Cent. (2370 degrees Fahr.) is considerably harder than the binary after such treatment. With subsequent heating at 400 degrees Cent. (750 degrees Fahr.), a slow but continuous rise in hardness takes place in the ternary alloy. To bring about hardening within a reasonable time, the binary alloy must be aged at a temperature in excess of 550 degrees Cent. (1020 degrees Fahr.). In fact, at 575 degrees Cent. (1065 degrees Fahr.) several hours elapse before any increase is observed. This so-called "incubation period" as shown in Fig. 15 is conspicuously absent in the time-hardness curve of the ternary composition aged at 400 degrees Cent. (750 degrees Fahr.).

Both the superior initial hardness as well as the seemingly decreased stability of the alpha solid solution in the ternary alloy might reasonably result from (a) lattice disturbance accompanying the allotropic transformation, and (b) large increase in grain boundary surface in this newly formed phase of small grain size.

An analogous case is possibly to be found in the effect of mechanical deformation on the precipitation hardening characteristics of certain alloys as reported by Harrington (4). An additional example of the stimulating influence of deformation is furnished by the binary iron-tungsten solid solution which after deformation in a supersaturated state will harden rapidly when heated to 400 degrees Cent. (750 degrees Fahr.).

That the tungsten concentration of the ternary solid solution has little effect upon the maximum hardness developed by precipitation treatment is evident from Figs. 17 and 18. Such lack of relationship constitutes another point of difference between the ternary and the binary series since, in the latter, maximum hardness rises with tungsten content, as clearly shown by Figs. 15 and 16. As was earlier observed, however, the resistance to softening during the later stages of the precipitation cycle at 600 or 700 degrees Cent. (1110 or 1290 degrees Fahr.) is notably superior in the ternary solid solutions of higher tungsten concentration.

Tests to Detect Presence of Retained Austenite

In an alloy of the type under consideration, the possibility of

austenite retention must be considered. Although the equipment for magnetic analysis was not available, three other methods were employed as described in the following paragraphs.

The X-ray diffraction pattern shown in Fig. 20 was obtained from the ternary alloy as air cooled after 30 minutes at 1400 degrees Cent. (2550 degrees Fahr.). The reflections are obviously those char-

Fig. 20—Diffraction Pattern from Ternary Alloy Air Cooled from 1400 Degrees Cent.

Table IV

Single Aging Versus Multiple Aging Ternary Alloy Air Cooled from Solution Treatment

Specimen (Pairs)	Solution Temperature Degrees Cent.	Solution Temperature Degrees Fahr.	Initial Rc	Aged at 400 Degrees Cent. (750 Degrees Fahr.) 1 Hour	2 Hours	5 Hours	25 Hours
0	1200	2190	46–46	47–47	47–48	49–49	51–51*
1	1200	2190	46–47	...	47–48	...	...**
2	1200	2190	46–46	...	...	48–49	...**
3	1200	2190	46–46	...	...	...	51–51**
0	1400	2550	37–39	42–43	44–45	45–46	48–49
1	1400	2550	37–39	...	44–45	...	...
2	1400	2550	38–38	...	...	45–45	...
3	1400	2550	37–38	...	...	...	49–50
				Aged at 500 Degrees Cent. (930 Degrees Fahr.)			
				15 Min.	30 Min.	1 Hr.	5 Hrs.
0	1200	2190	45–46	56–57	58–59	60–60	64–64
1	1200	2190	45–46	...	58–59	...	...
2	1200	2190	46–46	...	...	59–60	...
3	1200	2190	46–47	...	...	...	64–64
0	1400	2550	38–39	50–50	51–52	54–54	61–62
1	1400	2550	37–39	...	52–52	...	...
2	1400	2550	38–39	...	...	53–53	...
3	1400	2550	38–39	...	...	...	60–61

*Multiple Aging
**Single Aging

acteristic of the body-centered cubic solid solution. Small grain size and a fairly complete range of orientations are indicated. Absence of face-centered cubic reflections does not, of course, preclude the presence of a limited amount of austenite.

Cooling to subzero temperatures might be expected to transform appreciable quantities of residual austenite and result in measurable hardness increase. The "martensitic" alpha thus formed

should, furthermore, enhance the hardening during subsequent precipitation treatment.

The alloy as air-cooled from 1200 degrees Cent. (2190 degrees Fahr.) and from 1400 degrees Cent. (2550 degrees Fahr.) was immersed in liquid nitrogen without measurable effect upon the hardness. Specimens so treated were aged together with the untreated alloy at 400 and 500 degrees Cent. (750 and 930 degrees Fahr.). No significant hardness differences were observed.

Multiple aging treatments have been reported to result in the transformation of residual austenite in high speed steel (5). Although in this case the hardness may decrease slightly due to overaging at 550 degrees Cent. (1020 degrees Fahr.), volume changes and X-ray diffraction data supply evidence of the transformation.

The method of multiple aging was applied to the ternary alloy as air-cooled from 1200 and 1400 degrees Cent. (2190 and 2550 degrees Fahr.). As may be seen from the data of Table IV no positive effect results from this treatment.

If this ternary composition is modified by the presence of some 5 per cent chromium the subzero treatment results in an immediate rise of several points in Rockwell C hardness. During subsequent aging at 400 to 600 degrees Cent. (750 to 1110 degrees Fahr.), the hardening rate and the maximum hardness are likewise increased. This alloy, moreover, responds to multiple aging by developing a hardness considerably greater than that resulting from a single aging period of equal duration.

Upon the basis of these tests it must be concluded that the quantity of residual austenite present in the ternary alloy after cooling from the solution treatment is negligible.

Summary

A ternary alloy of 50 per cent iron, 30 per cent cobalt and 20 per cent tungsten is compared with a binary iron-tungsten alloy of like tungsten concentration in respect to hardening characteristics.

As cooled to room temperature from solution treatments at 1100 to 1400 degrees Cent. (2010 to 2550 degrees Fahr.), this alloy shows a hardness considerably in excess of that found in the binary alloy. The hardness decreases as the solution temperature is raised. Air cooling results in greater hardness than water quenching from

temperatures of 1100 and 1200 degrees Cent. (2010 and 2190 degrees Fahr.).

In the solution treated condition this alloy responds to precipitation treatment at a temperature some 200 degrees Cent. (390 degrees Fahr.) below that required by the binary alloy.

The so-called "incubation period" is not evident during aging at a temperature as low as 400 degrees Cent. (750 degrees Fahr.).

Maximum hardness appears to have little relation to the tungsten concentration of the solid solution, although the higher concentrations soften less rapidly with prolonged aging at 600 and 700 degrees Cent. (1110 and 1290 degrees Fahr.).

The presence of retained austenite is not established by any of the tests applied.

Bibliography

1. W. P. Sykes, "Precipitation Hardening in the Heavy Alloys," Symposium on Precipitation Hardening, American Society for Metals, 1939, p. 82.
2. K. S. Seljesater and B. A. Rogers, "Magnetic and Mechanical Hardness of Dispersion Hardened Iron Alloys," TRANSACTIONS, American Society for Steel Treating, 1932, Vol. 19, p. 553.
3. W. P. Sykes, "Structural and Hardening Characteristics of Some Iron-Cobalt-Tungsten Alloys," TRANSACTIONS, American Society for Metals, 1937, Vol. 25, p. 953.
4. R. H. Harrington, "The Role of Strain in Precipitation Reactions in Alloys," Symposium on Precipitation Hardening, American Society for Metals, 1939, p. 314.
5. Morris Cohen and P. K. Koh, "The Tempering of High Speed Steel," TRANSACTIONS, American Society for Metals, 1939, Vol. 27, p. 1015.

DISCUSSION

Written Discussion: By R. H. Harrington, research metallurgist, General Electric Co., Schenectady, N. Y.

This report of research conducted in the traditionally fine Sykes manner will require considerable time and study for true appreciation by the writer. Such a complete and thorough set of data always becomes another milestone along the path to understanding of precipitation hardening.

There are two or three minor points for discussion which do not at all detract from the value of the paper since they are mostly matters of opinion.

1. The writer believes it is confusing to speak of "austenite" with reference to such alloys whereas the author's use of the term "gamma phase" is simple and clear. The most common definition for "austenite" is that it is primarily a solid solution of carbon in gamma iron, with specific reference to the iron-carbon system.

2. The statement is made that "the precipitation hardening phenomenon in the case of the ternary alloy appears to lack the familiar incubation period." Since natural logic requires that each precipitation reaction, going to comple-

tion, must pass through this stage, the writer suggests that it might be better to state that no distinctly separate incubation period occurs for this alloy. All precipitation reactions in alloys preclude the necessity for local concentrations of solute atoms preceding true precipitation. It is only in a few alloys, such as the classical duralumin example, that this solute atom aggregation stage may be distinctly identified.

3. Considering Figs. 3 and 4, the structure obtained from a water quench from 1100 degrees Cent. (2010 degrees Fahr.) is compared with that for air cooling from 1300 degrees Cent. (2370 degrees Fahr.). Data in Fig. 2 indicate that water quenching from 1300 degrees Cent. (2370 degrees Fahr.) results in the same hardness as air cooling from 1300 degrees Cent. (2370 degrees Fahr.). It does not necessarily follow that the structures for both rates of cooling from 1300 degrees Cent. (2370 degrees Fahr.) will be the same. However, the writer believes it can be taken for granted that, although not so stated, Dr. Sykes has ascertained that, in this case, the structures are identical for the two rates of cooling from 1300 degrees Cent. (2370 degrees Fahr.).

Oral Discussion

J. C. SKINNER:[1] I wonder if there are any practical applications found for that, and what are the physicals?

Author's Reply

In reply to Dr. Harrington's discussion I might say that I used the term "austenite" only after some hesitation, and then only because I wished to emphasize the distinctly analogous relationship which exists between this alloy system and the iron-carbon system. I felt that such usage was justified by the definition of "austenite" appearing in the 1939 edition of the METALS HANDBOOK.

I agree with Dr. Harrington that the case of the incubation period might have been better described as one in which no "separate" incubation period is to be observed.

The microstructures shown in Figs. 3 and 4 were included to illustrate the decrease in amount of the residual second phase which accompanies an increase in temperature of solution treatment. The difference in structure resulting from difference in cooling rates is shown in Figs. 5 and 6. The etch darkened network appears to a greater or less extent in the microstructure of this alloy after air cooling from any one of the solution temperatures considered in this paper. If this results from the beginning of the Ar′ decomposition during the air cool, its effect upon the hardness is not evident when the solution treatments are carried out at 1300 and 1400 degrees Cent. (2370 and 2550 degrees Fahr.).

In reply to Lieutenant Skinner, I cannot say that this composition has ever found any commercial application. An alloy of slightly modified analysis has been used to some extent as a metal cutting tool, and in many cases showed a marked superiority over the standard high speed steels. This alloy, however, seemed to lack the toughness necessary for most commercial applications and consequently its use has been limited.

[1]Lieutenant, Air Corps Technical School, Director, Machine Shop Division, Chanute Field, Ill.

HOMOGENIZATION OF COPPER-NICKEL POWDER ALLOYS

By Frederick N. Rhines and Robert A. Colton

Abstract

A definition of the "degree of inhomogeneity" in a solid solution alloy in terms of two independent variables, a dimensional index and a concentration difference index, has been proposed. This concept has been applied to the case of the homogenization of copper-nickel powder alloys, and it has been shown that: (a) The time to reach a given degree of inhomogeneity during an annealing treatment is proportional to the square of the microstructural dimensions of the alloy, and (b) that the logarithm of the time to reach a given state is proportional to the absolute temperature of annealing. The progress of homogenization has been followed by means of electrical conductivity measurements. Methods for evaluating the indices of inhomogeneity as well as some practical applications of the concept have been discussed.

IN the course of the production of copper-nickel articles from mixtures of copper and nickel powders, it is customary to employ a heat treatment which serves two primary purposes: (a) to sinter, or weld, the powders into a solid mass and (b) to alloy the copper and nickel. Among the secondary effects of the heat treatment are the relief of work hardening, recrystallization, and frequently, grain growth. The sintering process normally progresses rapidly at the high temperature of the heat treatment, but homogenization (the alloying process) proceeds slowly at a rate diminishing with time, so that an even approximately homogeneous condition is rarely achieved in commercial practice. For this reason the length of the heat treatment is governed chiefly by the time required to attain an acceptable approach to a homogeneous state.

No entirely satisfactory measure of the degree of inhomogeneity in a solid solution alloy has as yet been devised. In practice the

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. Of the authors, Frederick N. Rhines is Assistant Professor, Department of Metallurgy and member of the Staff of the Metals Research Laboratory, Carnegie Institute of Technology, and Robert A. Colton, Research Assistant, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh. Manuscript received July 7, 1941.

heat treating times are usually selected by trial to give acceptable mechanical properties in the product without direct reference to the resulting structure of the metal. A more exact knowledge of the nature of the process of homogenization and of the physical properties that may be associated with various degrees of inhomogeneity should prove useful in establishing heat treating conditions. It is the purpose of the present research to study the first part of this problem: The nature of the process of homogenization in copper-nickel powder alloys to the end that its rates may be predicted.

Before examining the experimental observations it will be advisable to adopt a useful definition of the term "inhomogeneity." In its common usage, this word is qualitative and refers to no measurable quantity, but for the present purpose it will be useful to assign to it a metric property so that the "degree of inhomogeneity" in an alloy may be discussed. Among metallurgists it is customary to speak of more than one kind of inhomogeneity, such as; the coexistence of two or more phases in an alloy, or variations in the concentration of a solid solution from point to point; moreover, it is common to recognize a distinction between a micro-scale inhomogeneity within the micro-constituents of an alloy and a macro-scale inhomogeneity occurring as a gross concentration difference over a relatively large distance in a mass of metal. Obviously each of these usages refers to a different set of physical conditions and therefore requires a unique definition. It will be understood that the definition employed in the present case is intended to apply to micro-scale concentration inhomogeneity in solid solutions only. As a matter of convenience the term "micro-inhomogeneity" (as opposed to "macro-inhomogeneity") will be employed.

To describe a state of micro-inhomogeneity in a solid solution it appears necessary to recognize two principal variables: (a) the concentration difference and (b) the dimensions of the microstructure. This will be done by defining two indices of inhomogeneity, a concentration difference index (I_c) and a dimensional index (I_d).

A simple statement of the maximum concentration difference existing in an alloy does not in itself adequately define the state of micro-inhomogeneity even when the structural dimensions are also given. The variation in concentration between the two extremes may follow an infinite variety of courses so that it is necessary to take into account the form of the concentration variation. The initial form will be established by the composition and method of manu-

facture of the material. During homogenization the concentration differences tend to diminish through the operation of the diffusion process, and the components of the alloy will be distributed between the points of maximum and minimum concentration according to the form of a diffusion penetration curve (1)[1] which is subject to definition if the boundary conditions can be expressed. In other words, two alloys similar in the type of their concentration distribution at the start, although not necessarily similar in their micro-structural dimensions, will follow similar paths toward the homogeneous state, but at different rates. At a given degree of inhomogeneity in each there will be the same relative quantities of material of each distinguishable concentration between the maximum and minimum values. Two samples having the same form of concentration distribution will, by definition, be equally inhomogeneous with regard to the concentration difference index.

This statement provides a basis upon which (I_c) can be quantitatively defined. Suppose that a sample of an inhomogeneous alloy is cut up into small pieces (containing, for example, a hundred or a thousand atoms each), and that the composition of each of these cubic elements is determined. Then the deviation of the concentration of each element from the concentration which it would reach at the completion of homogenization (C_o) will be the difference between the concentration of the element (C_i) and the over-all concentration of the alloy (C_o), that is ($C_o - C_i$). This difference may be multiplied by the volume of the element (V_i), expressed as twice[2] the per cent of the total volume of the sample ($\frac{Vi}{V} \cdot 200$), to give a weighted value of the "deviation from homogeneity" of the particle. If the values for all of the elements in the sample are added the sum will give a figure ranging between 0, when the alloy is perfectly homogeneous, and 100 when the inhomogeneity is at a maximum. It should be noted that the dimensions of the microstructure do not enter into this definition of (I_c). Expressed in mathematical terms the definition becomes:

$$I_c = \sum \frac{Vi}{V} \cdot 200 \cdot (C_o - C_i)$$

where the difference ($C_o - C_i$) is always taken as positive.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

[2]The factor two is introduced simply to cause the possible values of (I_c) to occur in the convenient range 0 to 100 instead of 0 to 50.

It must be understood that values of (I_c) defined in this way may be compared directly only when the materials under comparison started from the same initial states, i.e., both are of the same composition and both were identically cast, or both were made from powders of the same compositions, or both have been subjected to the same mechanical treatment and so on. Because there are inherent in this concept no direct relationships among the states of inhomogeneity of materials of differing initial states, equality in the indices of inhomogeneity will be arbitrarily selected as the criterion of equivalent inhomogeneity among such unlike materials.

The dimensional index (I_d), expressing the distance between adjacent centers of maximum and minimum concentration, is difficult to define in a satisfactory manner, because of the specialized geometry of many alloy structures and because of the usually irregular macroscale distribution of the concentration differences (macro-inhomogeneity). For present purposes these complications will be ignored and (I_d) will be defined simply as the average of the distances between adjacent centers of maximum and minimum concentration.

Having thus adopted a definition of inhomogeneity in terms of two indices (I_c) and (I_d) it will now be possible to describe in a quantitative way the influence of several factors upon the rate of homogenization.

It appears reasonable to assume that the homogenization of a solid solution occurs essentially as a diffusion process. The rates of other processes in which diffusion is a major mechanism quite generally conform to the relationship (2).

$$\log \frac{x^2}{t} = \frac{a}{T} + b$$

where (x) is a length of reference over which diffusion is taking place, (t) is the time, (T) is the absolute temperature and (a) and (b) are related in various ways (depending upon the geometry of the diffusion system) with the diffusion coefficient (D) and the activation heat of diffusion (Q).[3] If this equation is applied to the case of homogenization (I_d) may be selected as a value of (x). Since the process of homogenization influences only the concentration gradients in an alloy and not the structural dimesions, (I_d) remains constant throughout the treatment,[4] i.e., retains its initial value.

[3]The constant (a) is, in fact, equal to $\frac{Q}{R}$; see reference 1.

[4]When a "perfectly homogeneous" state is reached (I_d), of course, ceases to have any meaning.

Perhaps the most obvious conclusion to be drawn from this equation is that the time is directly proportional to the square of the distance, which is to say that at any one temperature in a particular alloy the *time required to reach a given degree of homogenization (I_c value) from a common initial state will be directly proportional to (I_d^2)*. In practice this means that the time required to achieve a particular result in homogenization should be proportional to the square of the linear dimensions of the microstructure (the average distance between adjacent unlike centers). That this conclusion is in accord with the experimental facts will be demonstrated presently.

A second conclusion that may be drawn from the above equation, and is common to all diffusion processes, is that *for a given alloy with a specified (I_d) value the logarithm of the reciprocal of the time to reach a given degree of homogenization is proportional to the reciprocal of the absolute temperature.* This conclusion will also be shown to be in agreement with the experimental observations. The rate of homogenization may be expected to increase very rapidly with the temperature.

These two relationships are exact for solid solution alloys. On the other hand, as stated above, the present concept of inhomogeneity provides only an empirical basis for comparing the degrees of inhomogeneity among alloys of differing initial state and composition; their inter-relation cannot be handled exactly. Also the calculation of the degree of inhomogeneity from known values of the diffusion coefficient involves such complicated boundary conditions that no satisfactory mathematical expression for this purpose has yet been derived. The inter-relation of these factors will instead be handled, in a limited number of cases, by means of graphical approximations which will be described after the experimental data have been presented.

Experimental Procedure

The direct measurement of the structural dimensions (I_d) in an alloy can ordinarily be accomplished by metallographic means. There will usually be a rather broad range of values that may be read in any one sample partly because of an irregular arrangement of the structure and partly because a 2-dimensional section rarely traverses the shortest path between unlike centers in the space array. A rigorous calculation of the space dimensions from surface dimen-

Table I
Description of the Powder Alloys

Alloy No.	Copper Per Cent	Nickel Per Cent	Particle Size Expressed in Screen Size Maximum	Minimum	I_d in cm.
2	99	1	300	325	0.0124
3	97	3	300	325	0.0092
4	95	5	300	325	0.00802
5	93	7	300	325	0.0074
6	90	10	300	325	0.00676
7	80	20	300	325	0.00569
8	70	30	300	325	0.0051
9	60	40	300	325	0.00472
10	50	50	300	325	0.0044
11	40	60	300	325	0.00472
12	30	70	300	325	0.0051
13	20	80	300	325	0.00569
14	10	90	300	325	0.00676
15	7	93	300	325	0.0074
16	5	95	300	325	0.00802
17	3	97	300	325	0.0092
18	1	99	300	325	0.0124
2A	90	10	50	100	0.03465
2B	90	10	100	150	0.01955
2C	90	10	150	200	0.01377
14A	10	90	50	100	0.03465
14B	10	90	100	150	0.01955
14C	10	90	150	200	0.01377

sions in an ideal aggregate is possible, though difficult; no satisfactory method of taking into account a maldistribution of the structural parts is at present available. For this reason a technician's estimate of the (I_d) value, based upon the smallest distance between unlike centers that is found generally throughout a large area of sample is employed. When powder briquettes are made from powders of nearly uniform and known sizes reasonably satisfactory (I_d) values may be approximated without resort to a metallographic estimate.

In the present research the alloy briquettes were made of copper and nickel powders (massive grains) of carefully graded sizes, see Table I, selected by screening. Copper and nickel powders of identical sizes were mixed in various proportions to give an alloy series ranging from pure copper to pure nickel.[5] Under these conditions the value of I_d is a function of the composition of the mixture as well as of the particle size. The (I_d) values listed in Table I were computed by adding the radii of two unlike particles (copper and nickel) where the radius of the particle of the minor constituent of the mixture was that of the average grain size and the radius of the particle of the major constituent was taken as the radius of a sphere whose volume bore the same relationship to the volume of the

[5]The briquettes were prepared for us by the Metals Disintegrating Company of Elizabeth, New Jersey, and were stored prior to homogenization in evacuated glass containers.

minor particle as the ratio of the volumes of the two metals in the mixture.

To make a direct measurement of (I_c) it would be necessary to obtain a series of chemical analyses across a structural element of the alloy. This is not feasible with the techniques now available. An indication of the concentration distribution might be obtained indirectly in a number of ways: metallographically, by an X-ray determination of parameter and intensity values, or by the measurement of some property, such as electrical resistivity, which is sensitive to concentration differences.

Metallographic studies in which the color of the alloy or the response to a staining etch is used as an indicator of the local concentration have been unproductive in the present case because of the insensitivity of the method and the difficulties in the way of obtaining reproducible results.

X-ray methods also proved to be unmanageable with the equipment at hand. It was initially proposed to measure the concentration range in a partially homogenized alloy by measuring the range of parameter values covered by a single reflection in a Debye-Scherer film; corresponding degrees of micro-inhomogeneity, it was thought, would be represented both by similar line widths and by similar density distribution. It was hoped also that a reference point in homogenization might be established by the first clear resolution of the doublet. The sensitivity of the measuring devices available proved to be inadequate to distinguish between the structures of samples with heat treating times differing by a factor of as much as two, and the method was abandoned. Probably, this technique could be used if a sufficiently sensitive densitometer were available.

The electrical resistivity of an inhomogeneous alloy is quite sensitive to small changes in the concentration distribution. It was found possible to obtain a series of resistivity measurements during the course of homogenization of powder briquettes which were indicative of the relative (I_c) values; it is obvious that absolute values of (I_c) are not determined in this way.

Homogenization treatments were carried out in a thermostatically controlled furnace with a silica tube chamber with an atmosphere of tank hydrogen. The samples, which were received in the form of briquettes approximately $\frac{3}{16}$ x ½ x 1¼ inch, were placed in the silica tube while cold and hydrogen was introduced. The tube assembly was then placed in a furnace already at temperature. At the

end of a scheduled time interval the tube was withdrawn and allowed to cool before the sample was brought out into the air. It was found necessary to wait an hour or more after this, before making the resistance measurement, in order to permit dissolved hydrogen to escape from the alloy. After making the electrical measurements the sample was returned to the furnace for continuation of the homogenization.

Resistance measurements were made with the simple device illustrated in Fig. 1. The length over which the potential drop was measured was fixed by the permanent spacing of the needle contacts

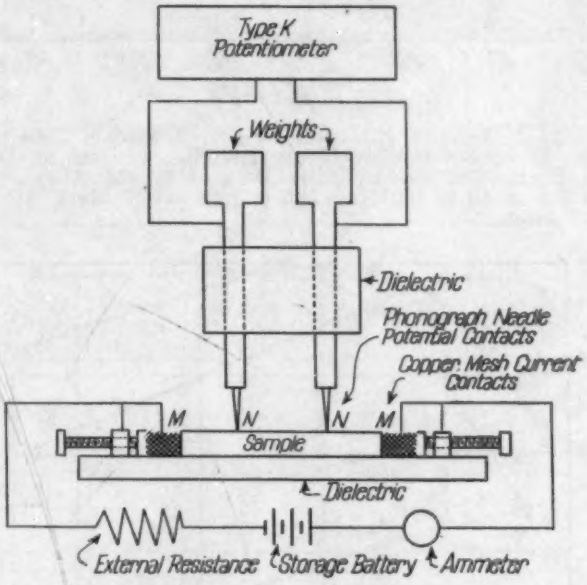


Fig. 1—Diagram of Apparatus Used For Electrical Resistivity Measurements.

(N), the current was adjusted to a constant value with an external resistance (R). By means of the adjustable current lead clamps the sample could be moved about so that a group of readings might be taken in various locations on the surface. As a rule four or more measurements, taken at different positions on the sample, were averaged to give each recorded relative resistance value. No attempt was made to convert the data to absolute resistance readings.

The results are presented in Figs. 2 to 9, where the relative electrical resistance has been plotted as a function of the time of homogenization. The forms of these curves are noteworthy; in the general case the resistivity at first rises, reaches a maximum and then decreases gradually to a constant value; in some cases only a decrease

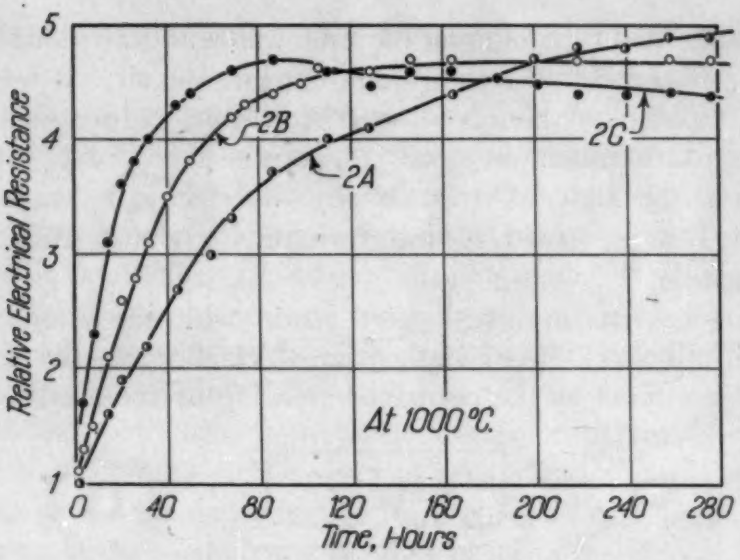


Fig. 2—Relative Electrical Resistance Versus Time For 90 Copper-10 Nickel Powder Briquettes Homogenized at 1000 Degrees Cent. The Powder Sizes Denoted by the Alloy Numbers Are: 2A = 50 to 100 Mesh, 2B = 100 to 150 Mesh, 2C = 150 to 200 Mesh.

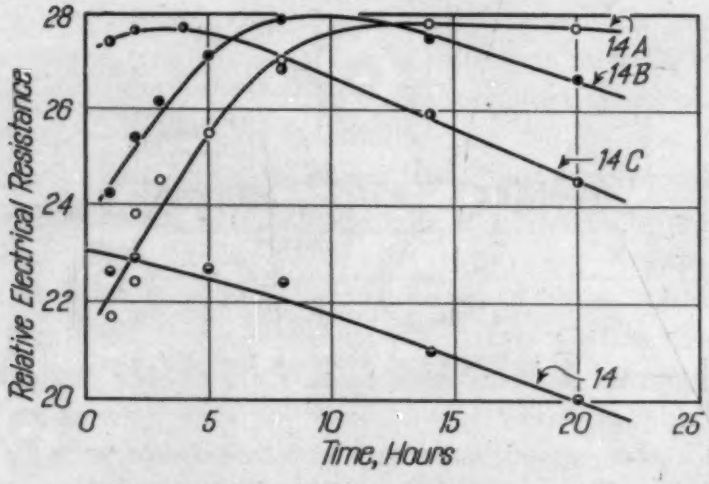


Fig. 3—Relative Electrical Resistance Versus Time For 10 Copper-90 Nickel Powder Briquettes Homogenized at 1000 Degrees Cent. The Powder Sizes Denoted by the Alloy Numbers Are: 14A = 50 to 100 Mesh, 14B = 100 to 150 Mesh, 14C = 150 to 200 Mesh, 14 = 300 to 325 Mesh.

in resistance is observed. There is reason to believe that the absence of an initial resistance rise in the latter curves is not real, for this effect was observed only at the higher heat treating temperatures where homogenization proceeds most rapidly and the period of increase could have been passed before the first resistance reading could be made. The curves corresponding to the alloy containing 50 per cent each of nickel and copper show no maximum. The

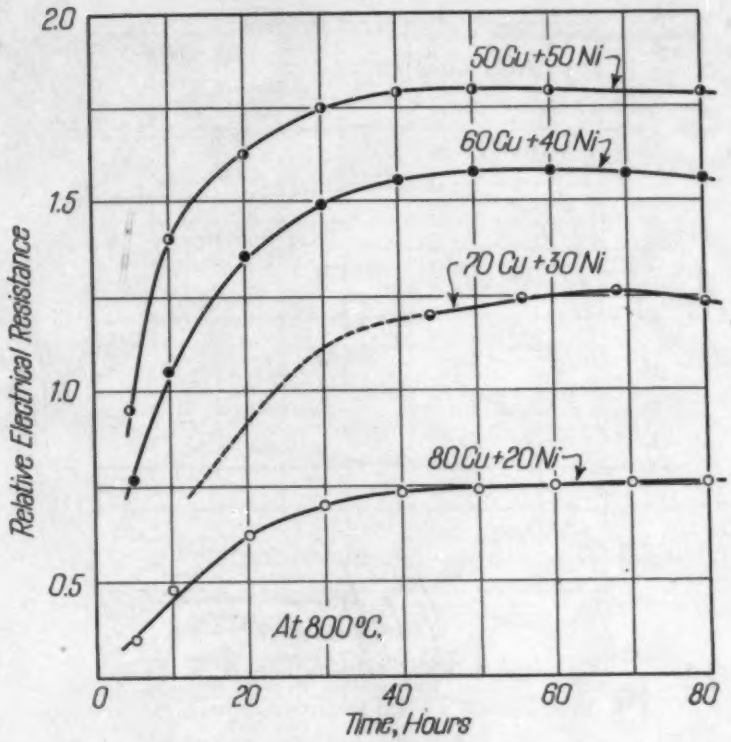


Fig. 4—Relative Electrical Resistance Versus Time For Powder Briquettes, Screen Size 300 to 325, Homogenized at 800 Degrees Cent.

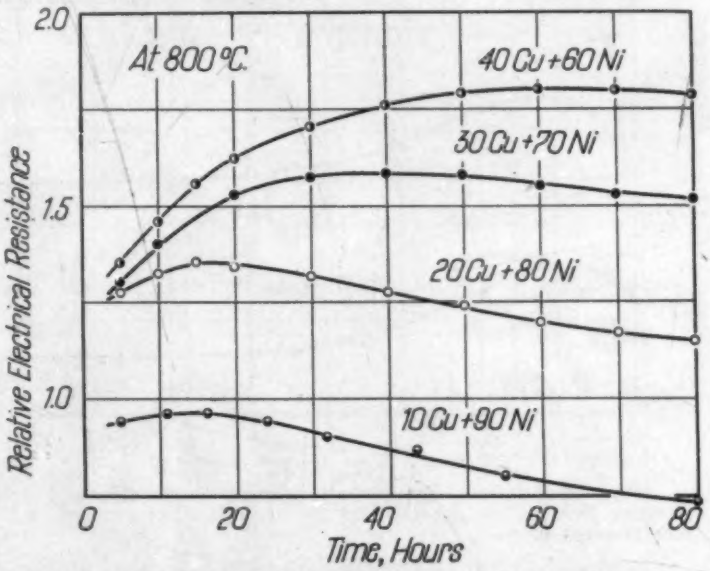


Fig. 5—Relative Electrical Resistance Versus Time For Powder Briquettes, Screen Size 300 to 325, Homogenized at 800 Degrees Cent.

probable reason for this will be discussed presently in this report.

As can be seen in Figs. 2 to 9, the resistance value of the maximum is almost identical among all of the samples of the same

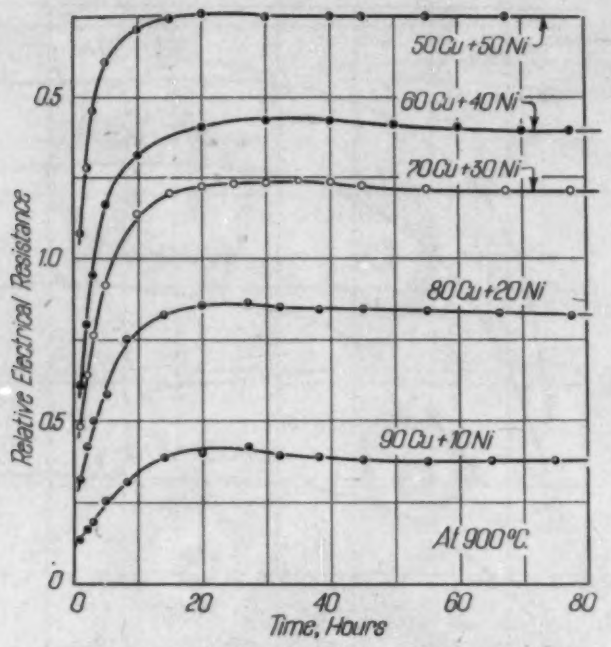


Fig. 6—Relative Electrical Resistance Versus Time For Powder Briquettes, Screen Size 300 to 325, Homogenized at 900 Degrees Cent.

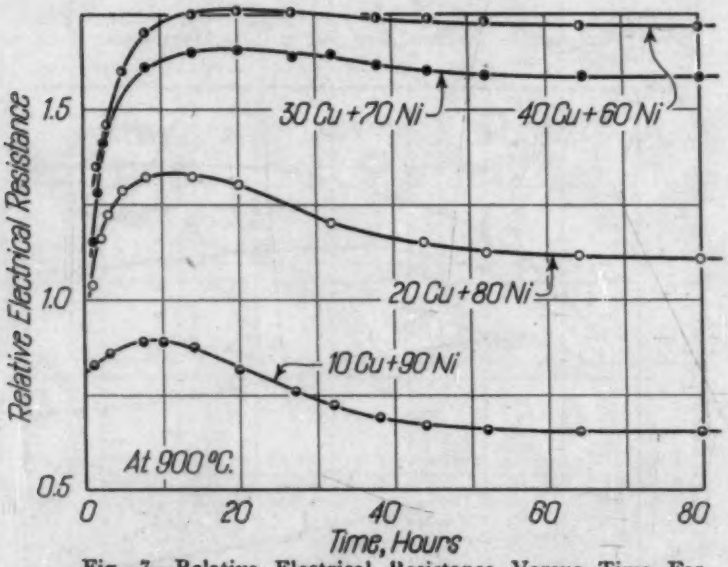


Fig. 7—Relative Electrical Resistance Versus Time For Powder Briquettes, Screen Size 300 to 325, Homogenized at 900 Degrees Cent.

composition regardless of the grain size or the temperature of homogenization. This is taken as evidence that the resistance curves for any one alloy composition pass through the same series of resistance values, although the times to reach specific values of resistance may differ. It has already been pointed out that the diffusion curves

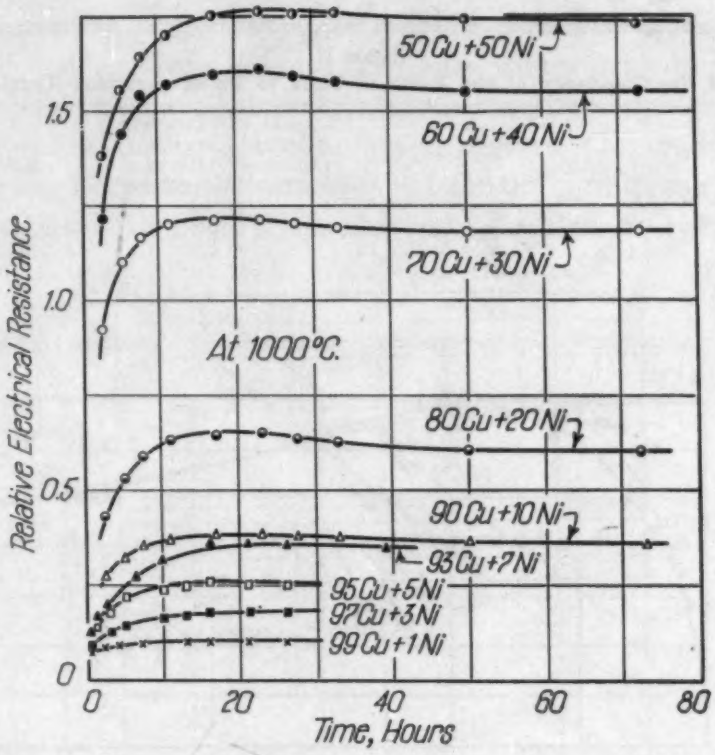


Fig. 8—Relative Electrical Resistance Versus Time For Powder Briquettes, Screen Size 300 to 325, Homogenized at 1000 Degrees Cent.

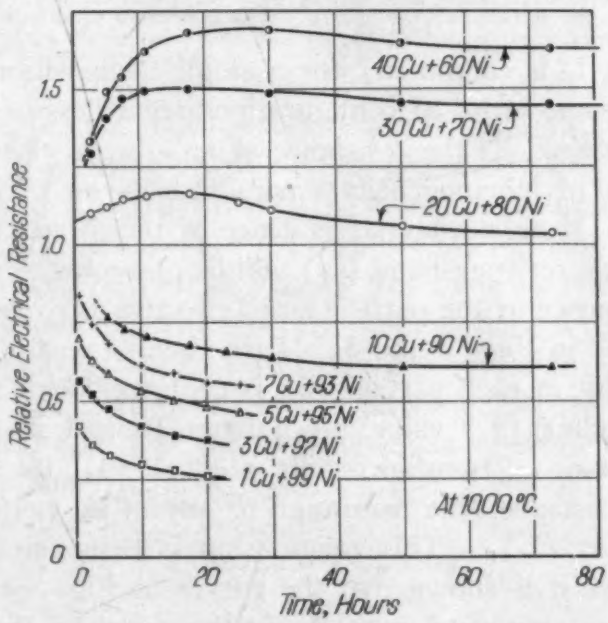


Fig. 9—Relative Electrical Resistance Versus Time For Powder Briquettes, Screen Size 300 to 325, Homogenized at 1000 Degrees Cent.

Table II
Test of the Constancy of the Ratio of Time to I_d^2 at Constant Temperature

Alloy No.	I_d^2	Hours at 1000 Degrees Cent. to Reach a Common Value of Electrical Resistance	Ratio of Time to I_d^2
2A	0.00120	18	15000
2B	0.00038	6.5	17100
2C	0.00019	2.5	13200
14A	0.00120	17	15800
14B	0.00038	8	21000
14C	0.00019	3	14200

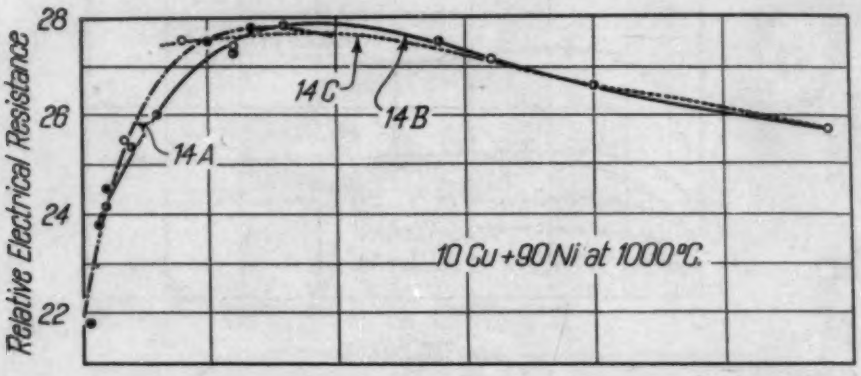


Fig. 10—Time-Resistance Curves of Fig. 3 Superimposed by Multiplying the Time Coordinates by the Appropriate Ratios of the (I_d^2) Values. This Demonstrates the Validity of the Conclusion That the Time to Reach a Given Resistance Value (Degree of Homogenization) at a Given Temperature is Proportional to (I_d^2). The Numbers Attached to the Curves Refer to the Alloy Number in Table I.

(from which I_c is computed) for a single composition should pass through the same series of configurations regardless of the temperature or grain size. If the resistance of an alloy is closely associated with the state of inhomogeneity a parallel behavior of this sort is to be expected. More substantial evidence of the direct connection between electrical resistance and (I_c) will be presented.

The influence of the particle size (effective I_d) is isolated in the data presented in Figs. 2 and 3. If the time to reach the maximum resistance value at each particle size is compared with the square of the corresponding (I_d) value, taken from Table I, it is found that a nearly constant relationship results, see Table II; the time to reach a common resistance (the maximum or any other value) is directly proportional to $(I_d)^2$. This relationship is demonstrated again in Fig. 10, where it is shown that the curves in Fig. 3 can be caused to superimpose simply by multiplying the times by the appropriate ratios of the $(I_d)^2$ values. Clearly the change in resistance with

homogenization is controlled directly by a diffusion process and a correspondence between (I_c) and resistance values is again indicated.

It has been predicted that for a given alloy the logarithm of the reciprocal of the time required to reach a given (I_c) value will be directly proportional to the reciprocal of the absolute temperature of homogenization. If this relationship is applicable, and if there is

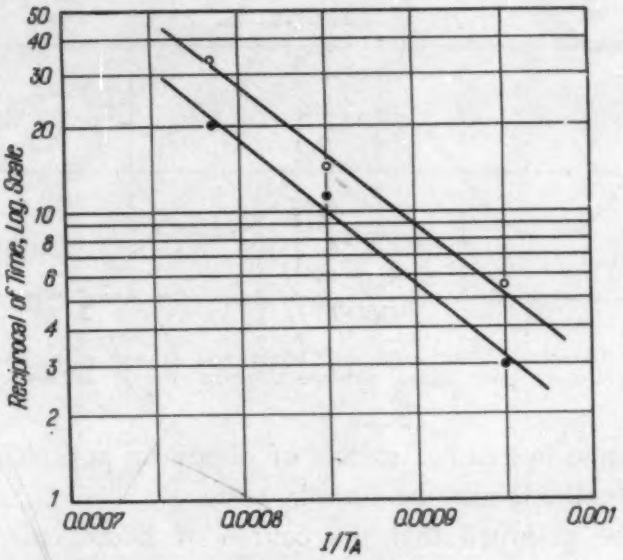


Fig. 11—Demonstration of the Linear Relationship Between the Log of the Reciprocal of the Time to Reach a Given Resistance Value (Degree of Homogenization) and the Reciprocal of the Absolute Temperature.

indeed a direct correspondence between (I_c) and the electrical resistance, then the logarithm of the reciprocal of the time to reach a given resistance in a particular alloy should be a linear function of the reciprocal of the absolute temperature. The data confirm this relationship; it can be seen in Fig. 11 that these variables plotted in the specified manner produce nearly straight lines. (The data exhibited in Fig. 11 produces better straight lines than do the alloys at some other concentrations; both positive and negative deviations occur. It is believed that macro-inhomogeneity in some alloys was responsible for this irregularity.)

Graphical Analysis

Thus far the relationships governing the rates of homogenization that have been discussed and the treatment of the data are orthodox.

In order to go further—in order to relate the (I_c) index with the diffusion coefficient and thus to determine absolute values of (I_c), to explain the form of the resistance curves, and to compare the (I_c) values among alloys of various compositions—it will be advantageous to adopt a number of simplified concepts. These are offered not with the idea that they will provide real solutions to the

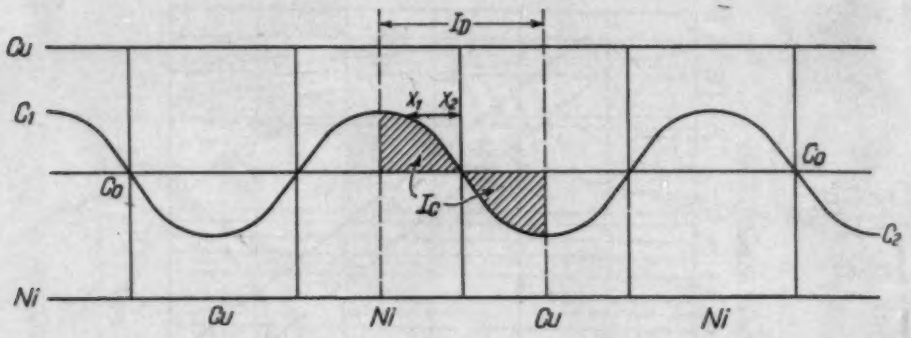


Fig. 12—Ideal Distribution of Copper and Nickel in a Thin Rod of Alternate Copper and Nickel Sections After a Period of Homogenization.

above problems, but rather means of obtaining approximate answers until better methods may be found.

Let it be assumed that the course of homogenization may be observed in a thin rod initially composed of alternate sections of pure copper and pure nickel, Fig. 12. After a period of homogenization the distribution of copper and nickel can be represented by the curve $C_1 - C_2$ where the concentration has been plotted vertically and distance horizontally along the bar. At the completion of homogenization the concentration curve becomes a straight line Co-Co. By definition the dimensional index (I_d) is the distance between the centers of unlike particles. The concentration index (I_c) is represented by the sum of the areas between the observed concentration curve $C_1 - C_2$ and the ultimate concentration curve Co-Co over a distance (I_d) regardless of sign; this is true only for the simple case cited. The exact form of the concentration-distance curve for short periods of diffusion can be obtained from the data of Grube (3), who measured the rate of diffusion in the copper-nickel system. Thus from Grube's data a time of diffusion can be associated with a specific (I_c) value for this simplified case. Diffusion curves corresponding to times greater or smaller than those used by Grube, and thereby (I_c) values for longer or shorter homogenization times, can be estimated from the given curves by applying the simple rule

that the square of the distance $(X_1 - X_2)$ between the interface and a given point on the concentration curve is proportional to the time of diffusion. These relations become inexact as (I_c) becomes small; under certain circumstances a better estimate of the form of the penetration curve and thus a better value of (I_c) could, perhaps, be obtained by using the tables of Stefan-Kawalki (4). By altering the relative lengths of the copper and nickel sections in Fig. 12 it is

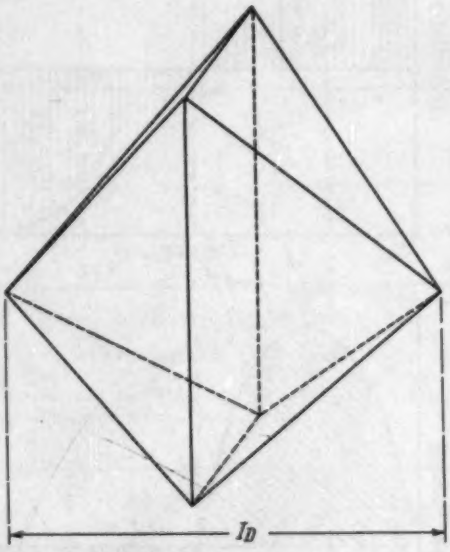


Fig. 13—Simplified Model of Space Within Which Diffusion Between Copper and Nickel Takes Place in a Powder Aggregate. The Apexes of the Double Pyramid Lie at the Centers of Adjacent Copper and Nickel Zones, and the Common Base Lies at the Original Copper-Nickel Interface.

possible to compare the forms of the concentration curves through a series of copper-nickel alloys. The curves corresponding to a given (I_c) value in the individual alloys of this series can be associated with their corresponding diffusion times so that times required to attain a similar degree of homogenization through the series of alloys can be obtained. This is the answer sought in practical homogenization, but it will be advisable to supply a more realistic picture of the diffusion system in an aggregate before attempting to compute the times for a real case.

A better approximation of the space within which diffusion is taking place[6] in a normal aggregate of powder particles is repre-

[6]Note—This type of figure can be made to fill space only when there are equal volumes of nickel and copper present, and so cannot be regarded as an acceptable approximation near the copper or nickel sides of the system; in the latter case a system of concentric spheres might better portray the geometry of the alloy.

sented in Fig. 13. Here the apexes of the double pyramid lie at the centers of adjacent copper and nickel grains (or zones), and the common base lies at the interface between copper and nickel. The value of (I_e) is no longer simply the area under the concentration-

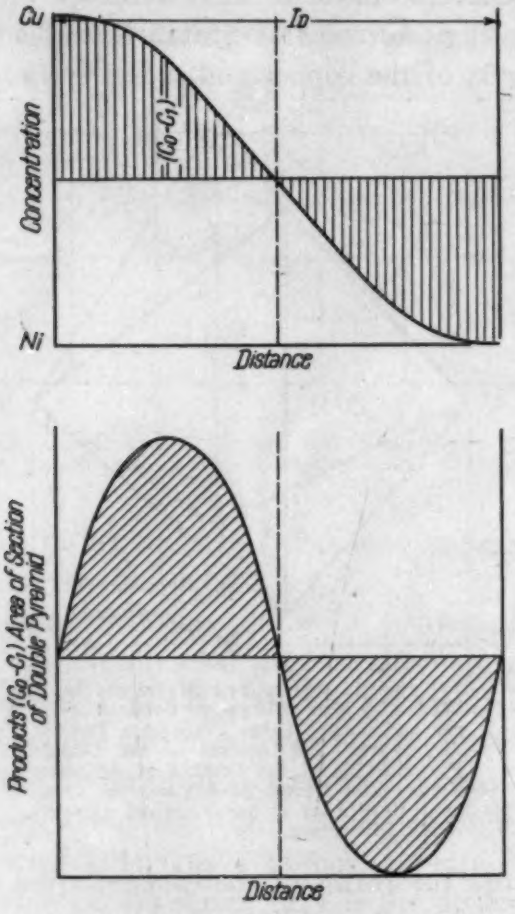


Fig. 14—Demonstration of the Method Used in Computing (I_e) From the Diffusion Penetration Curve. Values of (C_o-C_1), Regardless of Sign, Are Read From the Upper Figure and Are Multiplied by the Cross-Sectional Area of the Double Pyramid, Shown in Fig. 13, at the Corresponding Distance From the Interface. These Products Plotted Vertically in the Lower Figure at the Corresponding Positions on the Distance Scale Enclose an Area (Cross-Hatched) Which is Equal to One-Half of (I_e).

distance curve (as in Fig. 12), because the volumes of metal involved are not directly proportional to lengths upon the distance axis. Instead, the volumes are represented by a parabolic function diminishing to zero at the limits of (I_d). Thus, in order to compute (I_e) it is necessary to plot an auxiliary graph in which one axis is the

distance (I_d) and the other the product of (C_o-C_1), read from the concentration curves, and the area of a corresponding cross section of the double pyramid. Such a plot is given in Fig. 14. The shaded area represents (I_c). The curve shown represents the con-

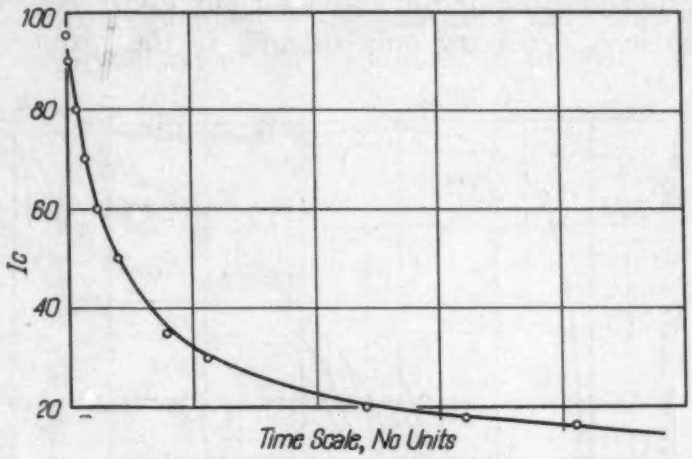


Fig. 15—Variation of (I_c) With Time For Alloy of 50 Per Cent Copper and 50 Per Cent Nickel. No Units Are Shown on the Time Scale Because These Vary With Temperature and (I_d); See Text.

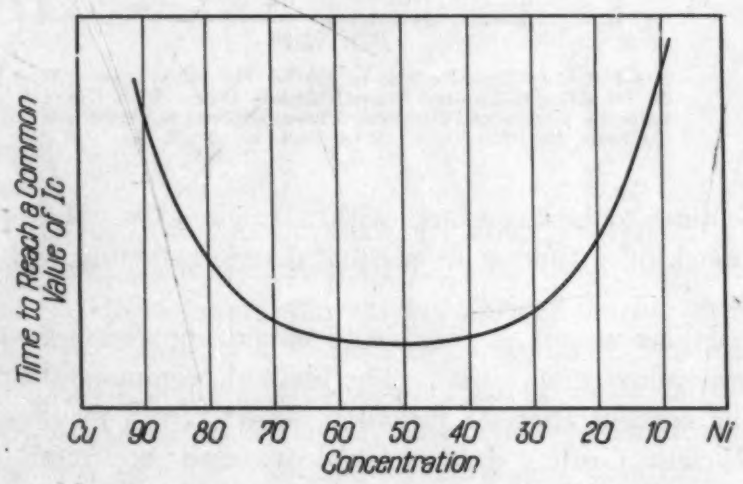


Fig. 16—Time to Reach a Common Value of (I_c) Versus Concentration of the Alloy For a Given Powder Size and Temperature. This Curve is Intended to Show the Form of the Relationship, But Cannot Be Used For Determining Absolute Values.

ditions obtaining in an alloy of 50 per cent copper and 50 per cent nickel after an hour at 1000 degrees Cent. (1830 degrees Fahr.). The total area under this curve gives an (I_c) value of 32. Thus it is seen that the alloy is about two-thirds homogenized in an hour at 1000 degrees Cent.

If a series of (I_c) values are computed in this way at a series of time intervals the value of (I_c) is found to vary in the manner shown in Fig. 15. Here absolute values of the time are not shown because it is desired to make the curve valid for all temperatures and particle sizes. In order to calibrate the graph for any given temperature and particle size it is necessary only to find, in the manner described

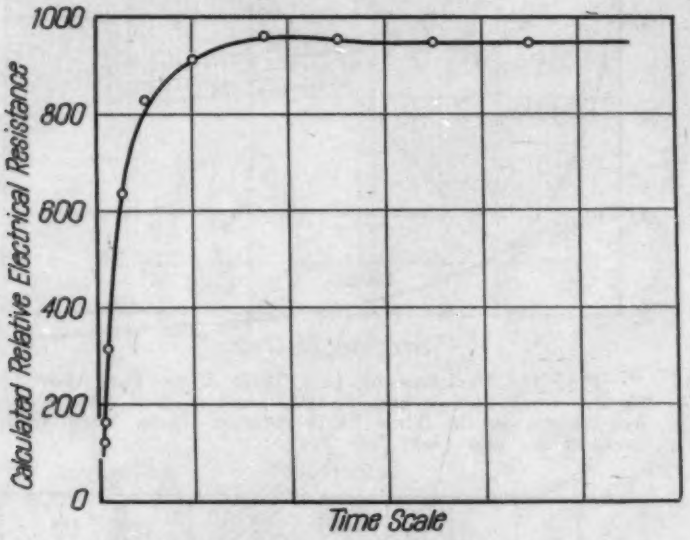


Fig. 17—Time-Resistance Curve For 70 Copper—30 Nickel Alloy Calculated From Diffusion Data. This Curve is to be Compared With the Corresponding Experimental Curve in Fig. 8.

above, the time to be associated with a single (I_c) value, plot this time and mark off a time scale in equal division starting with zero at the origin.

In a similar way it is possible to obtain approximate values of (I_c) for any alloy composition. The method becomes difficult, however, as the concentration of the alloy departs from the 50-50 composition, because Grube's data are inadequate for accurately predicting the forms of the diffusion curves when the interface departs from the 50-50 composition and when diffusion has proceeded to a point beyond which no substantially pure copper or nickel remains. For these reasons it has been found inadvisable to report here (I_c) values for other compositions, but the general form of the time to reach a given value of (I_c) as a function of concentration is shown in Fig. 16.

It will now be possible to relate (I_c) and the electrical resistance in a very approximate way. By virtue of the fact that the alloy

having the greatest resistance (50 per cent copper) forms a continuous network about the grains of the minor constituent metal during the early stages of homogenization it becomes reasonable to assume that a typical conductor element is represented by the model in Fig. 13. This assumption is approximately valid only when there are nearly equal volumes of copper and nickel present. The current

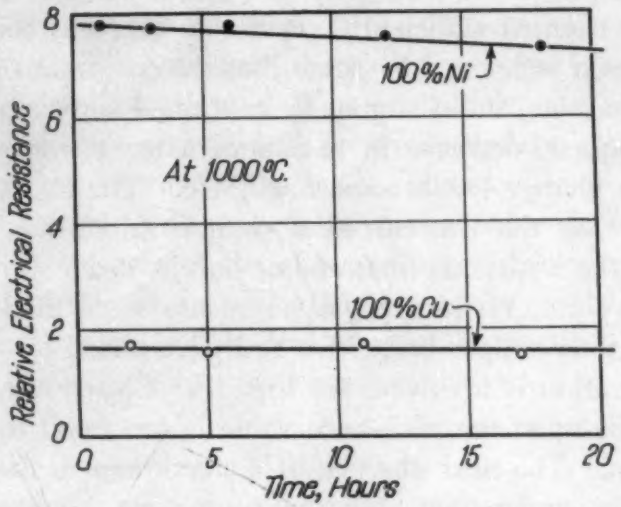


Fig. 18—Time Versus Electrical Resistance For Pure Copper and Pure Nickel Briquettes Homogenized at 1000 Degrees Cent. The Decrease in Electrical Resistance With Sintering is Seen to be Small.

may be assumed, for the present argument, to pass through the double pyramid from apex to apex. Under these circumstances the resistances of the various alloy layers formed during diffusion become additive. Thus it is possible to approximate the resistance of the alloy from a concentration-distance curve and a table of resistances of the copper-nickel alloys. The double pyramid of Fig. 13 is divided into a series of volumes by cutting it parallel to the base. The average composition of each volume is read from the corresponding diffusion curve, and the electrical resistance corresponding to this composition is read from a standard table of resistivity values. From these data the resistivity of each unit volume in a direction parallel to the length of the double pyramid may be computed. The total of the resistance values so computed is the approximate resistance of the double pyramid.

A series of relative resistance values calculated for an alloy of 70 per cent copper and 30 per cent nickel are plotted as a function

of time in Fig. 17. Although the resistance scale is obviously different from that used in obtaining the experimental measurements, it will be seen that the calculated and experimental curves are quite similar, i.e., both exhibit an initial resistance rise, a maximum and a slow decrease to a constant value. By adjusting the scales to superimpose these curves it should be possible to relate (I_c) with the experimental resistance readings; in the present instance the calculated curve is not deemed sufficiently precise to warrant this procedure.

It has been suggested by some that the maximum in the resistance curve may be caused simply by continued sintering of the alloy with a consequent decrease in resistance after the influence of the concentration change has become negligible. The above calculations demonstrate that the concentration changes alone are sufficient to account for the resistance maximum, but in order further to substantiate the point, resistance measurements were made during the annealing of pure copper briquettes and pure nickel briquettes where no homogenization is involved, see Fig. 18. Clearly the influence of sintering alone upon the resistance value is too small to account for the maximum. The near absence of a maximum in the 50-50 alloy can be readily understood, for the completely homogeneous alloy has about the highest resistance value attainable in the copper-nickel system.

Discussion

While methods of approximating the degree of homogenization to be expected in any copper-nickel alloy after a given heat treatment have been outlined above, these methods are cumbersome and the data here presented will probably be most useful when employed in simpler ways. For example: If it is found in practice that a given alloy has the desired physical properties after a certain homogenization treatment, the resistance may be measured and thereafter the reproduction of this resistance value can be used as a quick test of a satisfactory degree of homogenization; or, if it is desired to change the powder size or heat treating cycle but not the composition and degree of homogenization, the time required to reproduce the same resistance figure will be the time necessary to arrive at the same degree of homogenization with respect to the concentration difference index (I_c); or, if the heat treating conditions are known for a certain mix, but it is desired to alter the powder size or temperature

of heat treatment, the time required under the new conditions is easily computed from the two relationships stated in the text.

In the manufacture of powder metal articles, in order to promote good packing, it is customary to employ an assortment of particle sizes, instead of the very narrow range employed in the present research. It is evident that the most rapid homogenization rate possible with a given mixture will be realized when the particles of the minor constituent of the alloy are all of the smallest size appearing in the mixture. (This will give the smallest possible (I_d) value which corresponds to the most rapid homogenization rate.) Thus, it is advisable in making up a powder mix not to use the same assortment of particle sizes of both metals, but to use smaller particles of the minor constituent and larger particles of the major constituent.

The full usefulness of the concepts presented in this paper cannot be realized until the indices of inhomogeneity or the relative resistance values are related to the physical properties of the alloys. Future studies of these relationships are planned.

Summary

The concept of a "degree of inhomogeneity" in a solid solution alloy has been defined by describing two indices of inhomogeneity, a dimensional index (I_d), the average distance between unlike centers in an inhomogeneous alloy, and a concentration difference index (I_c), twice the sum of the products of the concentration difference from the total analysis and the percentage volumes of all of the distinguishable particles of metal making up the alloy.

It has been demonstrated that the time to reach a given state of inhomogeneity during a heat treatment varies directly as (I_d^2).

The logarithm of the reciprocal of the time to reach a given state of inhomogeneity is a linear function of the reciprocal of the absolute temperature.

A method for computing directly from diffusion data the approximate value of (I_c) after a given heat treatment has been proposed and demonstrated.

A laboratory method for determining (I_d) has also been described.

By means of measurements of the electrical resistance of powder alloys of copper and nickel, it has been found possible to follow the course of homogenization.

ACKNOWLEDGMENTS

The authors wish to acknowledge the use of data collected by Mr. Gordon Kimple and Mr. Robert M. Rood, who conducted portions of this research as senior thesis problems at the Carnegie Institute of Technology. Special thanks are due also to Mr. Don O. Noel of the Metals Disintegrating Company, who co-operated extensively in supplying samples and technical advice.

Bibliography

1. R. F. Mehl, "Diffusion in Solid Metals," American Institute of Mining and Metallurgical Engineers, Vol. 122, 1936, p. 11.
2. F. N. Rhines, W. A. Johnson and W. A. Anderson, "Rates of Internal Oxidation of Dilute Copper Alloys," *Metals Technology,* American Institute of Mining and Metallurgical Engineers, 1941. Also appears in other equivalent forms in: W. Seith, "Diffusion in Metallen," Julius Springer, Berlin, 1939. H. Weiss and P. Henry, *Comptes Rendus,* Vol. 171, 1920, p. 108; Vol. 173, 1921, p. 146; Vol. 174, 1922, p. 292; American Chemical Society, Vol. 19, 1923, p. 199; Vol. 20, 1923, p. 131; and elsewhere.
3. G. Grube and A. Jedele, *Zeit Elektrochemie,* Vol. 38, 1932, p. 799.
4. W. Jost, "Diffusion and Chemische Reaktion in Festen Staffen," Theo. Steinkopff, Dresden and Leipzig, 1937.

DISCUSSION

Written Discussion: By P. R. Kalischer, research laboratories, Westinghouse Electric and Manufacturing Co., E. Pittsburgh, Pa.

I have read the paper by Rhines and Colton with considerable interest. In general, I agree with the findings of their work but there are a few points that I believe could be clarified or on which more work could profitably be done.

The hydrogen atmosphere used in this work was "tank hydrogen" and I presume that no attempt was made to remove any oxygen or water vapor that may have been present as impurities. I have found that the usual tank hydrogen carries sufficient residual oxygen to form a heavy surface layer of oxide on copper, particularly at lower temperatures. If such a layer were to form it would materially lower the rate at which the voids present in the original compact are closed. This might account for a portion of the early high resistance characteristics.

Another point I would like to bring out is that in the sintering process there are a number of distinct processes going on simultaneously which should be evaluated separately.

First, there is the differential expansion of the two components which, particularly in the alloys near a 50 per cent copper, 50 per cent nickel composition might have a very pronounced effect on the porosity due to a loosening of the compact. This effect could have been evaluated by density measurements.

A second consideration is that during sintering as homogenization proceeds the resistance would be expected to increase as an approach is made to a solid solution but at the same time more area and continuity of metallic contact between the particles becomes available tending to reduce the overall resistance. If the effect of these opposed processes could be evaluated, by varying the current through the test piece, for example, it would materially clarify the picture of the overall sintering process.

A third point concerning which I would like to see further data is the change in relative resistance during the very early stages of sintering, the first two hours for example, since this time interval covers most normal commercial practice and it is in this range where a rapid and precise control test would be of value.

Written Discussion: By John F. O'Keefe, Moraine Products Division, General Motors Corp., Dayton, O.

This paper on homogenization of copper-nickel powder alloys by Dr. Rhines and Mr. Colton is a valuable contribution to the meager but growing literature on the subject of powder metallurgy.

In this investigation the authors have attempted to secure some fundamental data on the subject of diffusion of metals in powder form, a knowledge of which is essential for a more complete understanding of the sintering process.

The scope of their investigation was somewhat limited to a narrow field due to their elimination of an important variable encountered in commercial practice, that of particle size range. However, the limited range selected by the authors was covered very thoroughly.

Their results can be interpreted to mean that the sintering time reported to attain complete diffusion is the maximum time necessary when any particles of the indicated size are present. Any particles smaller than those indicated will, of course, diffuse in less time.

The authors have chosen an alloy series representing complete solubility in the solid state. Also the temperature has been chosen so that the range of alloys tested are in the solid state at all times. In commercial practice, some of the alloy combinations used contain a low melting constituent which forms a liquid phase in the earlier stages of the sintering operation. A notable example is the copper-tin alloy employed in the manufacture of porous metal bronze bearings. Also in this alloy series, there are a number of phase changes occurring as the tin diffuses into the copper. The Electrical Resistance versus Time curves for this series would probably be more complicated in appearance and interpretation than those described by the authors. Substantially complete diffusion, from a commercial viewpoint, is attained in much shorter times than was required with the copper-nickel powders. It has been our experience that decreasing the particle size of one of the constituents materially speeds the completion of diffusion.

Another important point noted in the paper was that the sintering and alloying actions are distinct processes. In the sintering of a single metal powder such as iron or copper, or a completely prealloyed metal powder, only the first action, that of sintering or bonding occurs, since homogeneity has been attained in the powder prior to sintering.

Authors' Reply

In reference to Mr. O'Keefe's discussion of the effect of particle size in the homogenization process I should like to point out that when increasingly smaller particle sizes are used (in a series of briquettes) the result is increased area of contact, and a smaller value for Id. The greater the area of contact between particles, the better are the diffusing conditions; the optimum conditions for a fast homogenization rate would probably be obtained with mixed particle sizes, with the larger particles the major constituent, and the smaller particles the minor constituent. This procedure has been suggested in the paper.

Mr. O'Keefe mentions a common commercial practice, that of sintering with a liquid phase present. We realize the practical importance of this kind of treatment; it presents a wholly different type of problem, one that requires an entirely different approach, than when diffusion occurs in the solid state alone. In this and, in fact, in any but complete solid solution systems, discontinuities will occur at the phase boundaries making interpretation of the resistance curves more difficult. We hope to make a study of this kind of homogenization at some later date.

In answer to Mr. Kalischer's remarks about the possibility of an oxide coating forming on the copper because tank hydrogen was used, we agree that this is possible. In view of the smallness of the resistance change when pure copper or pure nickel were annealed, however, we feel that this factor could not have had an important influence upon our results. The same argument is applicable in refutation of the contention that the ultimate fall in the resistance curves is caused by sintering; sintering, we agree, may be contributory, but not primarily responsible.

Although we noticed overall expansion and contraction of the briquettes in a qualitative manner, we made no actual density measurements.

In view of commercial sintering practice, Mr. Kalischer's suggestion that the first two hours of the sintering process be studied more carefully is well taken. Such a study could be most readily made on the copper side of the copper-nickel system, where the rate of homogenization is slower and therefore more amenable to measurements, but in any case would be difficult.

The authors wish to thank Mr. Kalischer and Mr. O'Keefe for their stimulating discussion.

STUDY OF DIMENSIONAL AND OTHER CHANGES IN VARIOUS DIE STEELS DUE TO HEAT TREATMENT

By G. M. Butler, Jr.

Abstract

Measurements of length changes undergone by a number of die steels during heat treatment showed that the new air hardening manganese-chromium-molybdenum steels could be treated so as to return exactly to their original lengths after drawing. Overheating or prolonged soaking caused shrinkage. Air hardening high carbon-high chromium steels showed only slight expansion, while oil hardening high carbon-high chromium steels expanded more than any of the other steels studied. Oil hardening manganese steels expanded considerably on hardening but shrank back almost to initial length after drawing. 5 per cent chromium-1 per cent molybdenum steels showed more expansion than any but the oil hardening high carbon-high chromium steels.

Three-dimensional measurements on blocks confirmed the low distortion of an air hardening manganese steel as compared with an oil hardening manganese steel and a 5 per cent chromium-1 per cent molybdenum steel. Along the grain direction, the latter two steels tended to expand, while the first-mentioned steel shrank.

An intimate relationship was found between length change and amount of retained austenite as measured by magnetic saturation studies. Minimum distortion was shown to correspond to a critical proportion of austenite. In the least deforming steels this proportion was attained by normal hardening; in the others, undesirable overheating was necessary for least length change.

Oil quenching was found to be applicable to certain air hardening steels but to have no marked advantages. Progress of austenite decomposition in hardened samples was followed after drawing at increasing temperatures.

THE purpose of this paper is to present the results of comparative studies of dimensional, hardness, and magnetic changes resulting from heat treatment of samples of various well-known tool steels used for dies, gages, and similar parts. Of special interest are observations on the behavior of some of the newer air hardening

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. The author, G. M. Butler, Jr., is research metallurgist, Allegheny Ludlum Steel Corp., Dunkirk, N. Y. Manuscript received June 19, 1941.

steels which are becoming increasingly popular because of their relative freedom from distortion and cracking during hardening and because of their lower hardening temperature and cost as compared with the high carbon-high chromium steels.

Most recent of such air hardening analyses is the manganese-chromium-molybdenum type, in which a low hardening temperature and air hardenability is obtained by the addition of 2 or 3 per cent managanese and 1 or 2 per cent of chromium and molybdenum to a 1 per cent carbon base. Included in this study were three commercial examples of this type, characterized by variations in the ratios of these three elements. Of interest is the extremely small dimensional change undergone by these steels when properly heat treated, and the effect of "grain" direction on the distortion of small blocks. The intimate relation between expansion and austenite retention as measured by magnetic saturation is herein emphasized.

Materials and Procedure

Seven varieties of die steels were included in this study. Besides the three air hardening manganese-chromium-molybdenum types already mentioned, tests were run on oil hardening manganese steel, 5 per cent chromium-1 per cent molybdenum steel, and two types of high carbon-high chromium steel. Emphasis was chiefly laid on comparison of a 3 per cent manganese air hardening steel with the oil hardening manganese steel and the 5 per cent chromium-1 per cent molybdenum type. The comparative behavior of these three has frequently been a subject of inquiry by tool steel users.

Table I
Bar Analyses of Steels

Type	Steel No.	C	Mn	Si	Cr	Mo	V
	A	0.89	1.61	0.25	0.13	0.32	
Manganese Oil Hardening	B	0.90	1.57	0.25	0.07	0.28	
	C	0.91	1.58	0.17	0.08	0.26	
5% Cr-1% Mo	D	0.98	0.42	0.17	4.62	0.86	0.07
	E	1.07	0.43	0.53	5.08	0.94	0.11
	G	1.01	3.12	0.27	1.23	0.98	
3% Mn Air Hardening	H	1.01	3.02	0.32	1.02	0.96	
	J	0.96	2.82	0.20	1.19	0.99	
High Carbon-High Chromium	K	2.04	0.26	0.26	12.27		1.09
(Oil Hardening)	L	2.16	0.25	0.34	12.37		1.07
High Carbon-High Chromium	N	1.53	0.31	0.25	11.75	0.77	0.65
(Air Hardening)	P	1.49	0.30	0.21	11.44	0.74	0.29
2% Mn-2% Cr-1% Mo (Air Hardening)	T	1.02	1.69	0.18	1.81	0.84	0.04
2% Mn-1% Cr-1% Mo (Air Hardening)	X	0.83	2.07	0.38	0.93	0.91	0.04

Two or three examples of each type of steel were included if available. An identifying letter was assigned to each individual lot of steel tested, to facilitate later reference. Chemical analyses of the actual bars are shown in Table I.

The major part of the program involved measuring length, hardness, and magnetic changes of short pieces of small diameter bars before and after hardening from various temperatures and also as drawn at the representative temperature of 375 degrees Fahr. (190 degrees Cent.). Additional work on three of the steels included determination of changes in these properties after cumulative draws at increasing temperatures, and study of dimensional changes occurring in blocks after a single recommended heat treatment.

Experimental Technique

Since the planned program involved heat treating and accurately measuring length, magnetic, and hardness changes in a large number of pieces, some effort was devoted to developing rapid and convenient means for treating and testing samples. Hardening had to be scale-free to avoid dimensional errors due to thickness of oxide layer, and heating had to be uniform to avoid warpage. Cooling, moreover, had to be carried out in the protective atmosphere used for hardening, at least for the air hardening steels, to avoid scaling during cooling. While there are now on the market furnaces designed for scale-free hardening of such steels, none was avaibale for this work.

Accordingly, it was finally decided to treat in nitrogen, using a nickel tube 1¾ inches internal diameter by 2½ feet long, sealed at one end, except for a small nickel pipe which entered there and returned along the outside of the tube. Tank nitrogen was fed through this pipe after passing through sulphuric acid and heated copper. The tube was heated in a small, automatically controlled Globar furnace for about 10 inches of its length, the balance extending out through insulating brick and wrapped at its outer end for a length of about 6 inches, with copper tubing soldered to the large nickel tube to allow rapid heat abstraction when cold water was passed through the copper tubing. The open end of the large tube was fitted with a cover plate held on by thumb screws and with a central hole about ½ inch in diameter. Through this hole passed a loosely fitting nickel pipe, on the end of which the sample holder

was mounted and through which thermocouple leads extended from the sample holder to the cold outer end and a suitable terminal plate.

The samples were 2 inches long by ¼ inch in diameter, from centerless-ground, annealed bars. With such small samples, a number could be treated simultaneously; so a holder was made like the rotating chamber of a revolver. This was made from a bar of 1⅝-inch round 17 per cent chromium stainless steel 2¼ inches long, with 10 equally spaced holes slightly over ¼ inch in diameter drilled circumferentially at a distance of ⅝ inch from the center, which was then drilled out with a ⅞-inch drill to reduce the mass to be heated. The handle side of the holder was closed with a thin disk to prevent samples dropping out, while the free end was open to permit samples to slide out quickly when quenching was desired. The sample holder and heating tube are shown in the photograph opposite.

One of the sample holes contained a dummy sample into which a 22-gage chromel-alumel thermocouple was inserted axially to the approximate center. The free ends of the couple were threaded with insulators and passed down through a hole into the nickel pipe handle and out to the cold end, as mentioned above. Thus the time at which the holder and samples reached the desired temperature could be noted, and the actual treatment temperatures accurately determined.

A thin metal baffle disk on the handle about 2 inches away from the holder promoted more uniform heating of the holder. As nearly as could be determined visually, there was very little gradient in temperature along the holder or the 10-inch heated length of outer pipe within which the holder was located, in such a position as to be at the center of the furnace. Hardness surveys along treated samples indicated consistent uniformity of hardening.

In use, the holder was filled with the samples to be treated, inserted in the cold end of the tube, the cover plate slid in along the handle and fastened in place, and nitrogen passed through at a rapid rate for several minutes. The holder and handle were then pushed into the heated zone, and observations of temperature were made on a portable potentiometer connected to the thermocouple leads. When the desired value was reached, the time was noted and samples held just 5 minutes at that temperature.

At the end of 5 minutes at temperature, the thermocouple leads were connected to a millivoltmeter indicator for convenience in read-

Heat Treatment Tube and Specimen Holder, with Specimens Partly Inserted and Extra Sample in Foreground.

ing falling temperatures, and the holder with its samples withdrawn into the water cooled outer end. Temperature readings were made every 15 seconds for the first minute, then every 30 seconds thereafter down to 500 degrees Fahr. (260 degrees Cent.), at which point the cover plate was removed and the samples dumped out to cool in air.

An effort was made to estimate how the cooling rates of the

group of samples in the water cooled zone compared with those of various sizes of round bar stock cooled in still air. 2-inch lengths of bar stock containing a thermocouple inserted into an axial hole half way through the piece were cooled in air from various temperatures. As nearly as could be judged, a ¾-inch diameter bar cooled in air at about the same rate as the samples in the tube, indicating that this was about the size of stock to which the expansion data contained herein would most nearly apply.

When samples were to be oil quenched, the cover plate was freed, the holder rapidly withdrawn from the hot zone, and the samples ejected by a quick shake into a basket which was immediately agitated in commercial quenching oil at room temperature.

Samples and Measurements

Samples were cut slightly over 2 inches long from annealed, centerless-ground bar stock of ¼ inch in diameter. Ends were beveled at 45 degrees on a lathe, then a surface grinder was used to finish the ends to 2 inches ± 0.002 inch long, with the flat portions about ⅛ inch in diameter and accurately parallel (within ± 0.0001 inch). Identification numbers were applied with an electric pencil; then all pieces were heated for 1 hour at 1200 degrees Fahr. (650 degrees Cent.) and air-cooled to relieve possible strains.

Lengths were determined with a Pratt & Whitney Electrolimit gage, using as reference standard a 2.000-inch piece supplied to check micrometers.

Magnetic saturation measurements were made with a Fahy Simplex Permeameter fitted with a pair of homemade adapters to permit use of short samples and a small 100-turn detector coil slipped over the sample. The field strength through the sample was in the neighborhood of 400 oersteds.

Rockwell C readings were made on a very narrow flat ground on one side of each sample after hardening. Samples were supported in a V-block.

Results

Figs. 1 and 2 give graphically the length, magnetic, and hardness measurements of all steels studied, as hardened and after the 375 degrees Fahr. (190 degrees Cent.) draw. Most of these values rep-

resent an average of two closely agreeing samples, though a few single samples were run to fill in extremes of some of the series.

In these graphs the bars represent the length measurements in terms of change in units of 0.0001 inch from the original 2-inch length. Values above the zero line indicate expansion, while those below mean shrinkage to less than the original length. The bar to

Table II

Summarized Average Length Changes of Steel Types Studied

Values are change in inches from original 2-inch lengths.
All pieces held 5 minutes at hardening temperature.

Steel Type	Cooled In	Hardening Temperature Degrees Fahr.	Hardening Temperature Degrees Cent.	As Hardened	After 375 Degrees Fahr. (190 Degrees Cent.) Draw
	Tube	1450	790	0.0010	0.0006
3% Mn-1% Cr-1% Mo	Tube	1500	815	0.0008	0.0002
	Tube	1550	845	0.0001	—0.0008
	Tube	1550	845	0.0021	0.0014
2% Mn-2% Cr-1% Mo	Tube	1600	870	0.0020	0.0010
	Tube	1650	900	0.0012	—0.0003
	Tube	1500	815	0.0022	0.0015
2% Mn-1% Cr-1% Mo	Tube	1550	845	0.0023	0.0012
	Tube	1600	870	0.0017	0.0001
Mn Oil Hardening	Oil	1425	775	0.0030	0.0011
	Oil	1475	800	0.0034	0.0010
5% Cr-1% Mo	Tube	1750	955	0.0023	0.0017
	Tube	1825	995	0.0022	0.0007
2% C-12% Cr	Oil	1825	995	0.0036	0.0027
	Oil	1900	1040	0.0038	0.0021
1.5% C-12% Cr-0.8% Mo	Tube	1825	995	0.0011	0.0005
	Tube	1900	1040	0.0015	0.0004

the left in each pair is the value as hardened, while the right-hand one is that after the 375 degrees Fahr (190 degrees Cent.) draw.

At the extremity of each bar is the Rockwell C hardness corresponding to that length, and below each pair of bars is a pair of dashed lines ending in circles, representing magnetic saturations as hardened and as drawn in terms of units of 1000 gausses. The increase in saturation due to the 375 degrees Fahr. (190 degrees Cent.) draw was in all cases very slight but consistent.

For convenient comparison, length changes are summarized in Table II. When more than one example of a single variety of steel was tested, the unweighted arithmetical average of the individual results is shown. The summary covers only the preferred cooling medium.

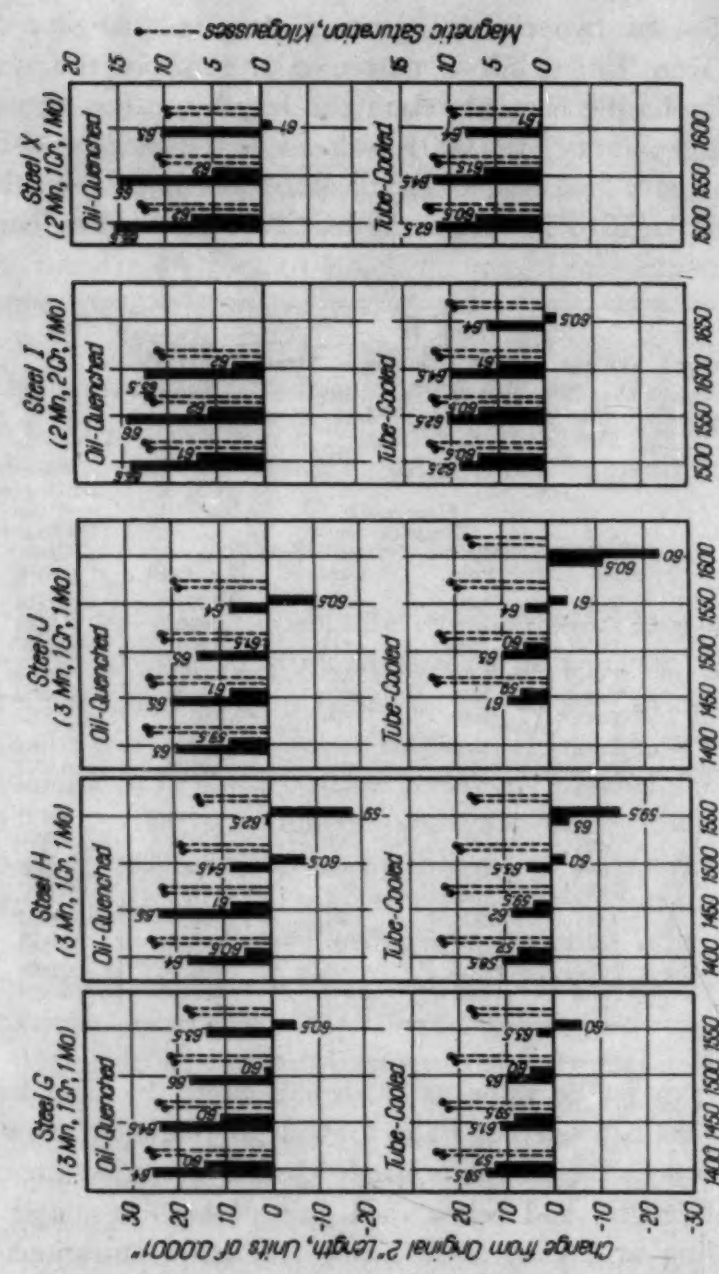

Magnetic Saturation, Kilogausses
Steel X (2 Mn, 1 Cr, 1 Mo)
Steel I (2 Mn, 2 Cr, 1 Mo)
Steel J (3 Mn, 1 Cr, 1 Mo)
Steel H (3 Mn, 1 Cr, 1 Mo)
Steel G (3 Mn, 1 Cr, 1 Mo)
Oil-Quenched
Tube-Cooled
Temperature, °F.
Change from Original 2" Length, Units of 0.0001"

Fig. 1—Effect of Various Hardening Temperatures upon Length, Magnetism, and Hardness of Several Air Hardening Manganese Steels. Held 5 minutes at Hardening Temperatures. Left-hand solid bar is change from original length as hardened; right-hand bar is change after drawing at 375 degrees Fahr. (190 degrees Cent.). Dot at end of broken line indicates magnetic saturation. Figures at tips of bars are Rockwell C hardnesses.

Manganese Steels

Oil Versus Air Hardening—Certain striking differences between the various types of steels are at once apparent. Most notable is the contrast between the older manganese oil hardening type and the newer manganese-molybdenum-chromium air hardening steels. The latter (Steels G, H, and J) expand less with rising hardening

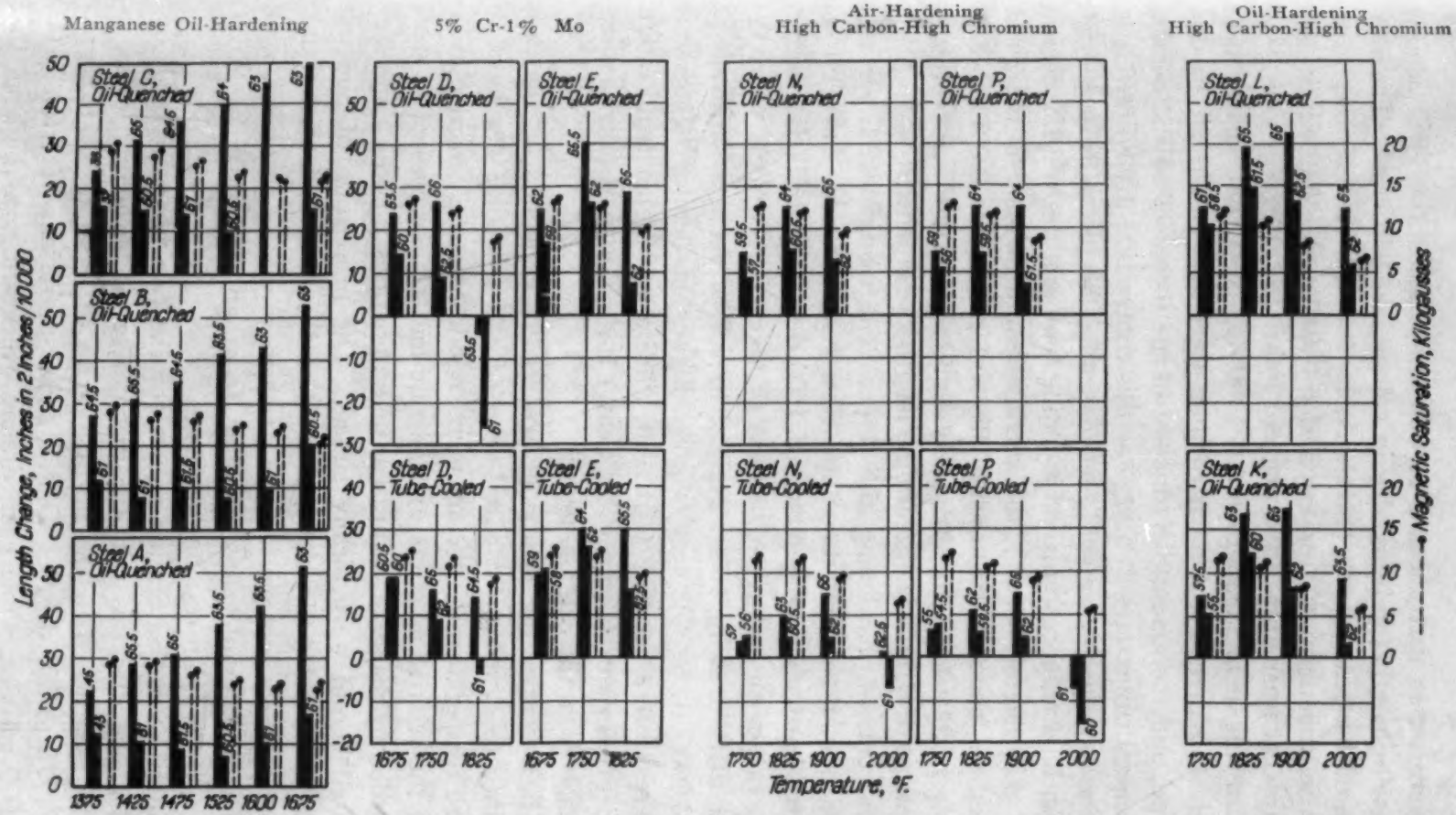


Fig. 2—Effect of Various Hardening Temperatures upon Other Steels Studied. Held 5 Minutes at Hardening Temperatures. Left-hand solid bar is change from original length as hardened; right-hand bar is change after drawing at 375 degrees Fahr. (190 degrees Cent.). Dot at end of broken line indicates magnetic saturation. Figures at tips of bars are Rockwell C hardnesses.

temperatures, so that above a certain temperature they will actually decrease in length (and probably in volume) as hardened. The manganese oil hardening type (Steels A, B, and C), on the other hand, shows increasingly greater expansion with rising hardening temperatures, at least up to 1675 degrees Fahr. (915 degrees Cent.).

Drawing at 375 degrees Fahr. (190 degrees Cent.) causes much greater shrinkage in the oil hardening steel than in the air hardening type, and the amount of this shrinkage increases as the quenching temperature is raised. Large as this contraction after drawing is, however, it is in no case sufficient to restore the pieces to their original length. At the customary hardening temperature of 1425 degrees Fahr. (775 degrees Cent.), the average length increase in the 2-inch samples was about 0.0030 inch. This was reduced to 0.0011 inch by drawing at 375 degrees Fahr. (190 degrees Cent.), which represents a shrinkage of 0.0019 inch from the length as hardened.

In contrast, hardening the 3 per cent manganese-1 per cent molybdenum-1 per cent chromium type (Steels G, H, and J) from the usual hardening temperature of 1500 degrees Fahr. (815 degrees Cent.) causes an average expansion of about 0.0008 inch, which decreases after drawing to an average of 0.0002 inch, a shrinkage of only 0.0006 inch. A very slightly higher hardening temperature would result in a net change of zero, while a still higher temperature, 1550 degrees Fahr. (845 degrees Cent.) for example, results in actual shrinkage from the original length.

These contrasting behaviors are readily explained on the basis of ability to retain on cooling some of the austenite developed at elevated temperatures. A convenient, nondestructive, sensitive measure of the relative amounts of austenite and ferrite present in steels is afforded by magnetic saturation determinations, to which the samples used herein were ideally suited. The proportion of austenite present is probably inversely proportional to the saturation value; at approximately zero gausses the structure is wholly austenitic, while at some maximum value, ranging from about 16,000 to 20,000 gausses, there is no residual austenite.

Study of the saturation values for the two types of steels discussed above discloses that the manganese oil hardening steels, A, B and C, hardened in the normal range of 1425 to 1475 degrees Fahr. (775 to 800 degrees Cent.), show saturations of from 13,000 to 15,000 gausses, while even drastic overheating, as high as 1675

degrees Fahr. (910 degrees Cent.), will not reduce these values below about 11,000 gausses.

In the air hardening steels, G, H, and J, magnetic saturations decrease more rapidly with increase in hardening temperature, from about 12,000 after 1400 degrees Fahr. (760 degrees Cent.) to about 8500 at 1550 or 1600 degrees Fahr. (845 or 870 degrees Cent.). This latter value corresponds to the presence of a considerable proportion of austenite, perhaps as much as 40 per cent.

Since austenite is denser than ferrite and occupies less volume per unit weight, the volume and length of a hardened sample will decrease as more of its mass is made up of the denser austenite. If a steel will retain considerable austenite, it should be possible, therefore, to select a hardening temperature such that the tendency to expand due to the transformation of some of the austenite to martensite is exactly balanced by the shrinkage due to the presence of the remaining, untransformed austenite.

Steels G, H, and J afford convincing demonstration of the validity of this reasoning. At a temperature which varies with composition from slightly above to slightly below 1500 degrees Fahr. (815 degrees Cent.), tube cooled samples show a net change of zero after drawing. It appears, moreover, that steels of this type hardened from this optimum temperature and drawn so as to return to their original length are characterized by magnetic saturation values in the range of 10,000 to 11,000 gausses, corresponding to perhaps 30 per cent of retained austenite.

This relationship between zero dimension change and magnetism is not confined to the single class of air hardening steel discussed above. This becomes evident by considering the data in the lower portion of Fig. 1 on similar steels with different chromium-manganese-molybdenum ratios.

The type represented by Steel T, with roughly 2 per cent manganese, 2 per cent chromium, and 1 per cent molybdenum, has a higher hardening temperature, as seen in Fig. 1; but after tube cooling from about 1650 degrees Fahr. (900 degrees Cent.), and drawing at 375 degrees Fahr. (190 degrees Cent.), it will return to its original length. Its magnetic saturation after this treatment is also about 10,000 gausses. It should be noted that the manganese content (1.69 per cent) of the particular heat represented in this investigation is considerably below the nominal 2 per cent, which

might account for the rather high hardening temperature. Longer holding at temperature allows a lower hardening temperature, as shown in a subsequent section.

Steel X is still a third modification, with 2 per cent manganese, 1 per cent chromium, and 1 per cent molybdenum. Its behavior is similar to the other manganese air hardening types. It returns to its original length after tube cooling from 1600 degrees Fahr. (870 degrees Cent.) and drawing at 375 degrees Fahr. (190 degrees Cent.), and its magnetic saturation then is just about 10,000 gausses.

While Steels T and X can be treated so as to have zero change from original length after drawing, yet their expansion as hardened, and therefore their shrinkage in drawing, is somewhat greater than that of the 3 per cent manganese steels, G, H, and J. This might be expected to correspond to an increased tendency of intricate shapes to deform during heat treatment.

5 Per Cent Chromium-1 Per Cent Molybdenum Type—Steels D and E are of this class of air hardening die steel, which has a considerably higher hardening range than the manganese-bearing types previously discussed.

Steel D is on the low side in all elements, while E is high in all elements. The total difference in alloy content is, in fact, nearly 1 per cent. This difference in analysis is reflected in a marked divergency in hardening characteristics. As shown in the upper middle portion of Fig. 2, Steel D hardens properly at slightly below 1825 degrees Fahr. (995 degrees Cent.) to give zero length change after drawing at 375 degrees Fahr. (190 degrees Cent.), while Steel E would have to be heated to perhaps 1900 degrees Fahr. (1040 degrees Cent.) to attain this same condition of minimum distortion. Steel D would have, like the steels of the manganese air hardening types, a magnetic saturation value of about 10,000 gausses as hardened and drawn to zero length change; while the saturation of Steel E may be estimated as somewhat less in its state of zero distortion.

In usual practice this type of steel would probably not be treated at temperatures as high as indicated here to be necessary for least distortion, because of possible grain coarsening. Therefore, it might be said to expand after hardening and drawing slightly more than the manganese air hardening steels. As noted later, longer soaking at temperature does not materially reduce the treatment temperature for least distortion.

High Carbon-High Chromium Types

1.5 Per Cent Carbon-12 Per Cent Chromium-0.75 Per Cent Molybdenum Air Hardening Type—Steels N and P represent two examples of this older, widely used die steel, which may be hardened in either oil or air. The high carbon-high chromium types are hardened in practice from quite high temperatures.

The lower middle portion of Fig. 2 shows the behavior of these steels in hardening. Evidently, under the conditions of these experiments, hardening temperatures in excess of 1900 degrees Fahr. (1040 degrees Cent.) would be necessary to yield the original length after drawing. As in the case of the 5 per cent chromium-1 per cent molybdenum steels, such high temperatures would seldom be used in commercial practice, due to a slight grain coarsening tendency which would generally be called "overheating". The residual expansion after treatment at lower temperatures and drawing is, however, less than for the 5 per cent chromium-1 per cent molybdenum steel; indeed, these steels are known for their nondeforming character.

Direct comparison is possible here with the results of Ameen.[1] On samples 5 millimeters round (0.196 inch) by 50 millimeters long (1.968 inch) of this type of steel, he obtained expansions as hardened which may be estimated from his graph (Fig. 6, measuring point 7) as being 0.04 per cent (0.0008 inch) after 995 degrees Cent. (1825 degrees Fahr.), and 0.095 per cent (0.0019 inch) after 1025 degrees Cent. (1875 degrees Fahr.). Corresponding values from Table II of the present paper are 0.0011 inch after 1825 degrees Fahr. (995 degrees Cent.) and 0.0015 inch after 1900 degrees Fahr. (1040 degrees Cent.). This seems to be rather close agreement between the work of two independent investigators.

2 Per Cent Carbon-12 Per Cent Chromium-1 Per Cent Vanadium Oil Hardening Type—Steels K and L are from two different lots of this hard abrasion-resistant steel, so extensively used for dies to give long runs.

The lower part of Fig. 2 reveals that this steel is not the equal of the more modern steels as regards nondeforming propensities. In fact, its expansion, both as hardened and after drawing, is greater than that even of the manganese oil hardening steel represented by Steels A, B, and C, at least in its preferred hardening range of 1800

[1]Einar Ameen, "Dimension Changes in Tool Steels During Quenching and Tempering", Transactions, American Society for Metals, Vol. 28, 1940, p. 484.

to 1850 degrees Fahr. (980 to 1010 degrees Cent.). It can be so treated as to return to its original length as drawn, but its grain structure would be seriously coarsened by the necessary heating to over 2000 degrees Fahr. (1095 degrees Cent.).

Oil Quenching Versus Tube Cooling

As Figs. 1 and 2 show, additional sets of samples of all the nominally air hardening steels were hardened in oil to compare with those hardened by cooling in the tube.

Such comparison discloses at once that in all cases the oil-quenched samples show greater dimensional change as hardened than the corresponding tube cooled samples. They also contract more on drawing, however, so that the net change as drawn at 375 degrees Fahr. (190 degrees Cent.) may be equal to or smaller than for the tube cooled pieces.

Of the manganese-chromium-molybdenum air hardening steels, it is worthy of note that oil quenching allows the use of lower hardening temperatures, which at the same time result in slightly higher hardnesses. Thus, the 3 per cent manganese-1 per cent chromium-1 per cent molybdenum steel, as represented by Steels G, H, and J, hardens adequately as low as 1400 degrees Fahr. (760 degrees Cent.) and best at about 1450 to 1500 degrees Fahr. (790 to 815 degrees Cent.), with smaller dimensional changes than the oil hardening manganese type (Steels A, B, and C).

This does not of itself mean that oil quenching parts made of air hardening steels, G, H, and J, would be good practice. It must not be forgotten that one of the fundamental reasons for resorting to a steel which does not require liquid quenching to harden is to minimize distortion and danger of cracking.

Distortion of a steel piece which has been hardened is a phenomenon made up of two factors. An attempt has been made in the work described in this paper to isolate and study one of these, namely, dimensional changes due to causes inherent in the nature of the steel and dependent on the relative proportions of retained austenite and of martensite from transformed austenite. The other factor is that of deformation caused by nonuniform stress distribution due to differences in cooling rate within the steel piece. This latter factor is a function of the rapidity with which heat is abstracted from the

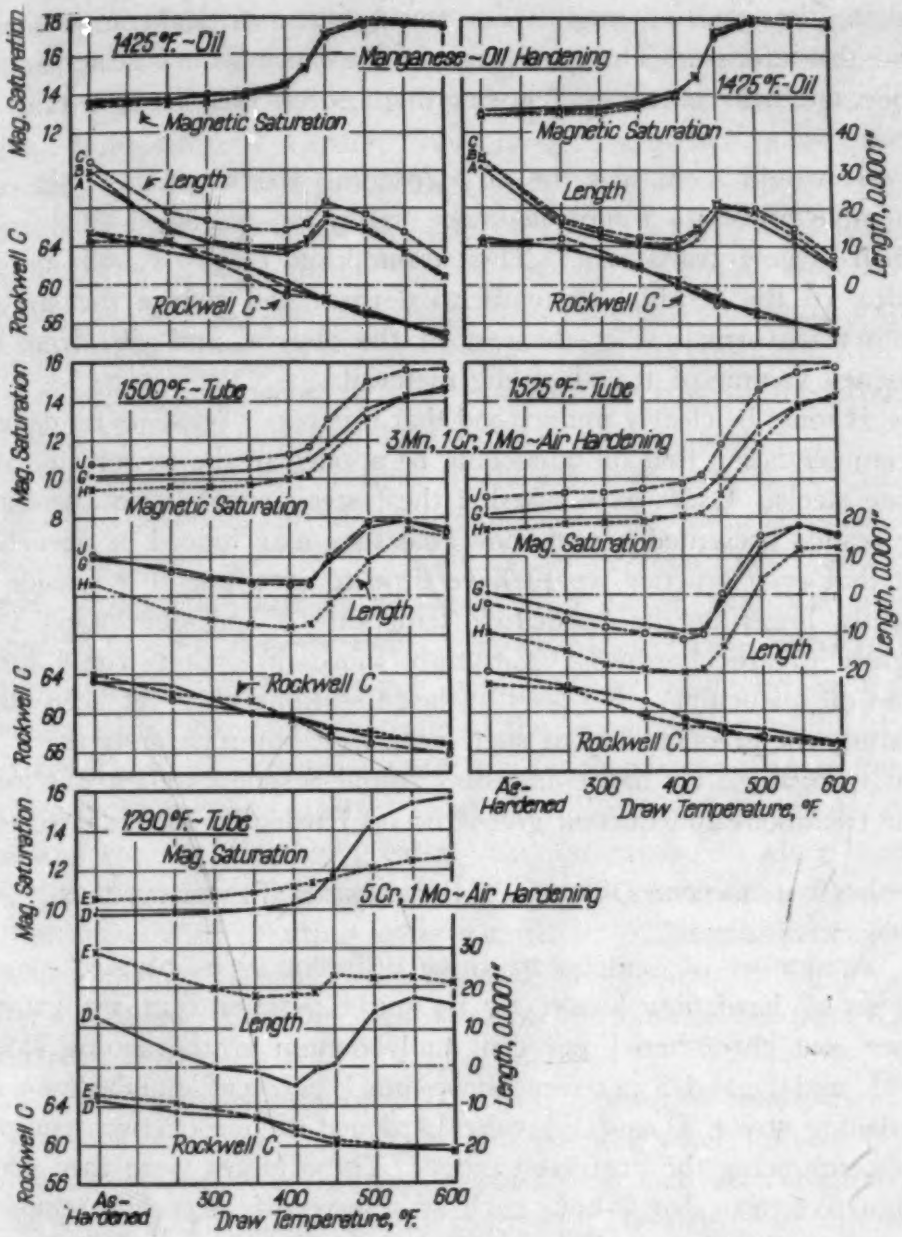


Fig. 3—Cumulative Draw Series.

piece and is partly independent of the nature of the steel, in that this type of distortion occurs in all types of steels, whether hardenable or not. When, however, a critical transformation range is encountered during cooling, the shrinkage due to cooling is opposed by expansion due to austenite decomposition. In a large piece cooled slowly, as in air, this reversal of stresses takes place at very nearly the same time throughout the piece; but if it were more rapidly

cooled, the exterior might pass through the critical range sooner than the interior. Thus one area in the piece would be expanding while another contracted, causing high stress gradients within the steel.

It would seem that the air hardening steels which retain considerable austenite might be more safely oil-quenched than steels which largely transform. This assumption is based both on the ability of the residual austenite to deform and reduce the stresses from transformation of the rest of the matrix, and also from the lessened volume of transforming material.

It must be clearly understood that this paper presents no definite recommendation that oil quenching be applied to the newer air hardening steels. Users have asked if these steels could be so quenched; the results presented herein show that they may indeed be quenched, but that such practice would have little to recommend it outside of slightly lowering the hardening temperature and developing very slightly greater hardness. Certainly more distortion would result from oil quenching. No tests on large sections have yet been made to study the practicability of such treatment, but apparently the 3 per cent manganese air hardening steel would respond well to the same heat treatment and quench given the oil hardening manganese steel.

Cumulative Draws at Increasing Temperatures

A number of samples of three different types of steel (manganese oil hardening steels, A, B, and C; 3 per cent manganese-1 per cent chromium-1 per cent molybdenum air hardening steels, G, H, and J; and 5 per cent chromium-1 per cent molybdenum air hardening steels, D and E) were hardened at one or two temperatures embracing the preferred range. These pieces were then given cumulative draws of 1 hour each at a series of ascending temperatures from 250 degrees Fahr. (120 degrees Cent.) up to 600 degrees Fahr. (315 degrees Cent.). After each draw the length change, magnetic saturation, and hardness were determined before submitting the samples to the next higher draw.

The results are shown graphically in Fig. 3, which sets forth the behavior after two different hardening treatments of Steels A, B, C, and G, H, and J, and after only one treatment of Steels D and E.

The two hardening temperatures have resulted in almost identical

sets of curves for the manganese oil hardening steels, with only a very slight shift downward in magnetic saturation after the higher temperature. A pronounced decrease in length after the 250 degrees Fahr. (120 degrees Cent.) draw is followed by more gradual shrinkage up to 400 degrees Fahr. (205 degrees Cent.), with no marked increase in magnetism. At 425 to 450 degrees Fahr. (220 to 230 degrees Cent.), austenite decomposition suddenly accelerates, causing a sharp increase in magnetism and corresponding expansion in length. From 500 degrees Fahr. (260 degrees Cent.) on up, this secondary expansion falls off due to tempering of the products resulting from the complete disappearance of austenite.

The course of the changes in the other two types of steels is somewhat different, in that austenite decomposition becomes significant at about 450 degrees Fahr. (230 degrees Cent.) and continues through a wider range, reaching a stable condition only at about 550 to 600 degrees Fahr. (290 to 315 degrees Cent.). Generally the length changes are paralleled by magnetic saturation changes. Likewise the magnitude of the secondary expansion at 450 degrees Fahr. (230 degrees Cent.) is much greater than in the oil hardening manganese steels. In almost all cases the secondary expansion was considerably greater than the expansion after hardening. Its magnitude, moreover, increased with elevation of hardening temperature, with resulting lower magnetism. The maximum length reached during drawing was, however, no greater or slightly less after hardening from the higher temperature, since the pieces were shorter as hardened.

The extreme difference in behavior of the two examples of the 5 per cent chromium-1 per cent molybdenum steel (Steels D and E) is interesting as revealing to what extent analysis variations are reflected in length and magnetic changes. The degree of difference seems abnormally large and will be studied further on more samples of this steel. The effect may be explained, however, on the basis that the greater concentration of ferrite-retaining, carbide-forming elements in Steel E make more difficult the retention of that austenite necessary for minimum dimensional change. The magnetic saturation values seem to confirm this hypothesis.

Obviously Rockwell hardness determinations completely fail to reflect any hint of the strong effect of austenite decomposition at

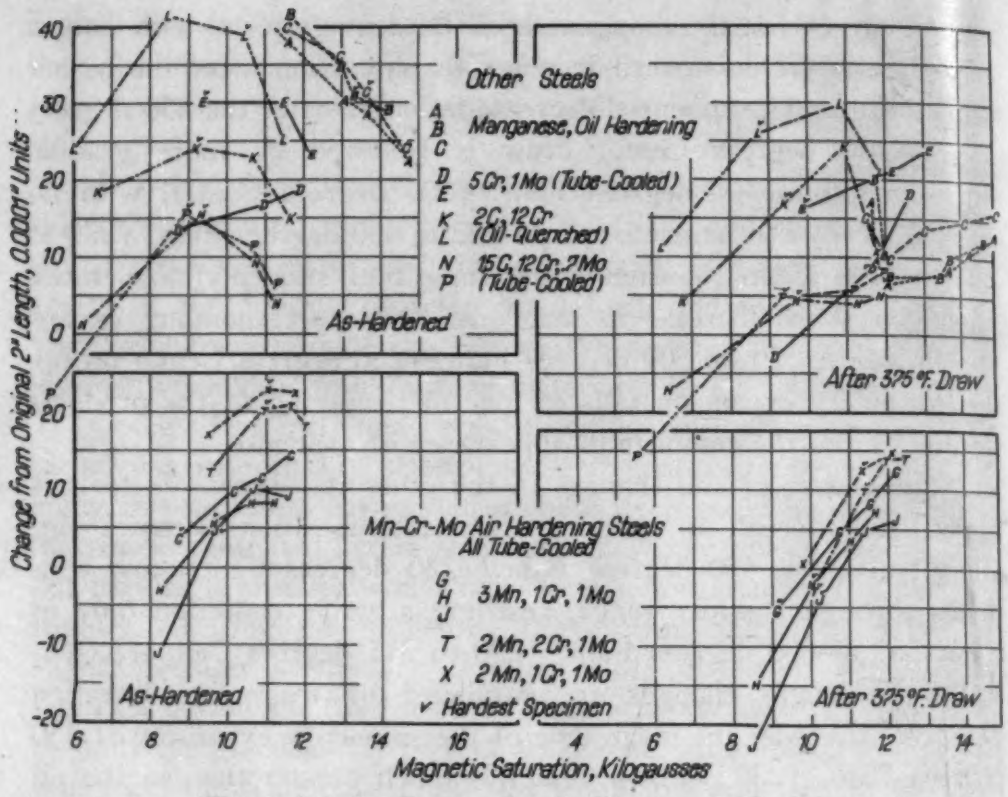


Fig. 4—Relation Between Length Change and Magnetism.

425 to 500 degrees Fahr. (220 to 260 degrees Cent.). This has been noted by other workers.

Other studies have shown, on the other hand, that the range of secondary expansion is clearly defined by impact tests.[2] Tempering up to 400 degrees Fahr. (205 degrees Cent.) results in increasing toughness, which reaches a sharp maximum at 400 degrees Fahr. (205 degrees Cent.) and drops again thereafter in the range of 450 to 500 degrees Fahr. (230 to 260 degrees Cent.). Therefore, tempering temperatures above 400 degrees Fahr. (205 degrees Cent.) should be avoided.

When tempered at 400 degrees Fahr. (205 degrees Cent.) or lower, both the 5 per cent chromium-1 per cent molybdenum and the managanese air hardening types have higher impact toughness than the oil hardening manganese steel; indeed, Izod values may be 50 per cent greater. Perhaps this is attributable to the presence of the retained austenite.

[2]A more comprehensive discussion of this correlation appears in the volume, "Functions of the Alloying Elements in Steel," by E. C. Bain, American Society for Metals, 1939, p. 281-287.

Relationship Between Dimensional Change, Magnetic Saturation, and Hardness

The data in Figs. 1 to 3 indicate clearly that magnetic saturation measurements, hardness, and length changes during heat treatment are intimately related. The nature of this relationship is more easily seen when length change is plotted as a function of magnetic saturation, as in the four parts of Fig. 4.

The manganese air hardening steels occupy the lower portion of this figure; the left-hand portion was plotted from the measurements as tube cooled, while the right-hand set of curves represent the values after drawing at 375 degrees Fahr. (190 degrees Cent.). Similarly the upper sets of curves depict the results for the other steels studied, as hardened in recommended fashion (oil quenching for Steels A, B, and C, K, and L; tube cooling for D and E, N, and P), and after 375 degrees Fahr. (190 degrees Cent.) drawing. The sample in each series which developed maximum hardness is indicated by a check mark above it.

Most of the steels as hardened display a peak in expansion within fairly narrow saturation limits characteristic of the individual steel types. In most cases this coincides with the hardness maximum. One marked exception is the 3 per cent manganese air hardening steels, G, H, and J, in which maximum hardness occurs down on the left slope of the curve, not far above the zero length change line. This makes them uniquely valuable as nondeforming steels. Another notable exception is the manganese oil hardening group (Steels A, B, and C), which display no peak at all; at higher quenching temperatures the curves merely continue almost linearly steeply upward to the left, out of the field of this graph. In this group maximum hardness occurs at much higher saturation values than for the other steels, at about 13,500 gausses.

Both 2 per cent manganese air hardening steels develop maximum hardness at their expansion peak, which occurs at a saturation value of about 11,000 gausses. All the other steels studied show maximum hardness in a range which would probably be 9000 to 10,000 gausses if points sufficiently close together were determined.

After tempering at 375 degrees Fahr. (190 degrees Cent.), the position of the curves and the hardness maxima have not changed much with respect to saturation—they have merely moved downward along the length change ordinate. The 2 per cent manganese

air hardening steels, X and T, have come down almost into the range of the 3 per cent manganese steels, while the peak in the air hardening high carbon-high chromium steels, N and P, has been flattened out.

The curves for oil hardening manganese steels, A, B, and C, show the greatest shift in position. Instead of sloping upward in the direction of greater expansion with decreasing magnetism, after drawing they slope downwardly to lower expansion as magnetism decreases. At about 12,000 gausses, however, this tendency is abruptly reversed, in that slight further decrease in magnetism is accompanied by drastic increases in expansion. This part of the curve is derived from seriously overheated samples; from 1525 degrees Fahr. (830 degrees Cent.) (saturation of 12,000 gausses) upward, grain coarsening beyond any acceptable commercial degree is acting to modify the expansion behavior. Since the other steels herein studied are much less susceptible to grain coarsening and retain relatively fine grain size after heating a hundred degrees or more above their optimum hardening range, the effect of grain size has been very slight for any of the other steels discussed herein. Coarsening could alone seem to account for the sudden expansion increase in the above-mentioned overheated pieces, in view of the smooth trend of the other measured properties.

As previously noted, the intersection of the zero change line and such curves as cross it occurs at 10,000 to 11,000 gausses for the manganese air hardening steels as drawn, and somewhat lower for the higher alloy types, which generally descend to zero change only after treating at temperatures above their normal range.

Dimensional Changes at Room Temperature

While no deliberate effort was made to study changes in untempered hardened pieces at room temperature, yet on several occasions it was observed that such changes occurred. For example, a group of samples of the oil hardening manganese steels, A, B, and C, after quenching from 1600 and 1675 degrees Fahr. (870 and 910 degrees Cent.) were measured as usual on the day following treatment, with results which were incorporated into Fig. 2. Two days later these samples were measured again, just before tempering, and all were found to have contracted 0.0005 to 0.0006

inch from the previously measured expansions of 0.0043 to 0.0053 inch.

A similar but smaller contraction was found in a lot of samples of Steels G, H, and J (3 per cent manganese-1 per cent chromium-1 per cent molybdenum) hardened from 1400 degrees Fahr. (760 degrees Cent.), regardless of whether they were oil-quenched or tube-cooled. When, however, these steels and the other air-hardened steels tested were hardened from the normal hardening temperature or above, thus retaining more austenite, they showed a slight but consistent increase in length on standing.

Such movements in cold, untempered pieces are probably responsible for the not infrequent cracking or actual rupturing of hardened articles of steel which have been allowed to stand for a while at room temperature before drawing. Stresses set up in hardening may have been safely below the danger point, but the additional stresses set up by this gradual room temperature movement made the total stress too great to resist.

Effect of Longer Times at Hardening Temperature

All of the foregoing tests and conclusions were based on behaviors of samples held in the furnace for only 5 minutes after they had reached the desired temperature. With this treatment, several of the steels developed best hardnesses only after heating to temperatures somewhat higher than those generally recommended.

Actual commercial die hardening often requires much longer heating periods because of the longer masses of metal involved. The exterior portions of the die may be actually up to temperature for rather prolonged intervals of time.

Additional tests were, therefore, made on almost all of the steels in the earlier program, to find out whether longer heating at the hardening temperature would make significant differences in the hardening characteristics.

An additional steel of each of the high carbon-high chromium types and of the 5 per cent chromium—1 per cent molybdenum type was included in these tests and the results incorporated in the averages. The added steels behaved very much as did the original steels and served to confirm the earlier observations.

New samples of all steels were soaked for 1 hour at temperatures used in the earlier work. An intermediate soak of 15 minutes was

also used in a number of cases in which the effect of soaking time seemed considerable. Samples were tube-cooled except for those grades for which oil quenching was customary.

Tables III and IV show the results obtained with the original 5-minute treatment and the later 15-minute and 60-minute treatments. All values are averages of data from three examples of each type, except that only one example of each of the air hardening 2 per cent manganese types was available.

The longer soaking times affected the behavior of the manganese air hardening steels to a pronounced degree. As Table III shows, lengths decreased as time at temperature became longer. Whereas the original 5-minute treatments showed that 1500 degrees Fahr. (815 degrees Cent.) gave proper hardness with minimum length change for the 3 per cent manganese variety, yet longer soaking at this temperature caused appreciable shrinkage, and this effect was aggravated at 1550 degrees Fahr. (845 degrees Cent.). Retention of more austenite was reflected in lower hardnesses and magnetism.

These undesirable results were, however, not evident when the hardening temperature was lowered to 1450 degrees Fahr. (790 degrees Cent.). Even an hour's soaking gave excellent results.

The 2 per cent manganese air hardening steels behaved similarly. The best hardening temperature for each was shown to be lowered drastically as soaking time was lengthened.

It seems reasonable to argue that demonstrating the effect of longer soaking times on small samples is at least roughly indicative of the effect that might be produced by using larger samples, with necessarily more prolonged heating. If this is acceptable, then an important generality may be proposed, on the basis of the foregoing results:

"When hardening various sizes of parts made from the new air hardening manganese steels, the heat treating temperature should be lowered as the thickness of the sections increases so as to necessitate longer soaking times." Thus for small pieces, use short heating times in the upper part of the recommended temperature range, but with heavy sections use long soaks at temperatures near the lower extreme of the range.

This rule applies only to a slight extent to the other steels discussed in this paper, most of which seem quite insensitive to prolonged heating, at least as far as these tests apply. The oil hardening manganese steels, for example, expanded only slightly less after

longer heating followed by drawing; the only feature of the extra time was a slight improvement in hardenability at 1375 degrees Fahr. (745 degrees Cent.).

The same responsiveness to somewhat lower hardening temperatures was found to be true of all the rest of the steels. After longer soaking the optimum results were in general obtained at temperatures in agreement with those commonly recommended.

It is important to note here that throughout this paper the optimum hardening temperatures are regarded as those giving best hardnesses after quenching and drawing. With some steels this coincides with the minimum length change; this is true of the air-hardening manganese and the air hardening high carbon-high chromium types, and essentially valid for the oil hardening manganese steel. The balance of the steels cannot be hardened to minimum dimensional change without overheating to such an extent that excessive amounts of austenite are retained. This is demonstrated by the magnetic measurements and sustained by the falling off of hardness.

Thus the form of test herein used suggests that only the manganese air hardening types can be so hardened and drawn as to return exactly to their original lengths and still develop proper hardness. The air hardening high carbon-high chromium steels will, if somewhat overheated, return to their original length after drawing and show good hardness, but the amount of retained austenite, as shown by magnetic measurements, is probably somewhat too great. If treated and drawn at the usual temperatures, these steels will show a very slight but consistent length increase. This slight expansion also characterizes the oil hardening manganese type.

The 5 per cent chromium-1 per cent molybdenum steels all showed a moderate degree of expansion when treated for best hardness. By slight overheating, they could be made to return to their original lengths after drawing, but excessive amounts of austenite were retained.

The steels which expanded most were those of the oil hardening high carbon-high chromium type, which could not be brought down to their original lengths even by moderate overheating and drawing.

Three-Dimensional Distortion Studies

The foregoing experiments were all confined to measurements

of a single dimension in a thin rod. Practical applications of die steels, however, usually involve larger masses, which are subject to dimensional changes in all directions. Fortunately, this study of distortion could be extended to cover simple 3-dimensional movement because of accessibility within the organization of a fully equipped die shop splendidly adapted for precision machining and measuring. Blocks of three types of steels included in the linear change studies were heat treated and dimensional changes accurately determined.

These steels were the 3 per cent manganese air hardening type, the 5 per cent chromium-1 per cent molybdenum air hardening type, and the manganese oil hardening type. Samples of the first two of these types were made from the same lots as studied for length changes; that is, the 3 per cent manganese type was represented by Steel G and the 5 per cent chromium-1 per cent molybdenum type by Steel E. A bar of analysis identical to Steel C was used for the oil hardening type.

From annealed bars 2¼ inches square, twelve blocks were cut as pictured in Fig. 5. The direction of the longitudinal axis or "grain" of the original bar was marked on each sample. These blocks were machined and ground down to the finished dimensions indicated in the sketch, with a stress-relieving draw at 1300 degrees Fahr. (705 degrees Cent.) applied before final grinding. Samples were measured with an Electrolimit gage. The final grinding was done so well that in only a very few cases did the spread of readings on any pair of parallel faces reach or exceed half a thousandth of an inch; most were within 0.0002 inch.

Blocks were hardened in a controlled atmosphere furnace yielding clean, scale-free, decarburization-free surfaces. Soaking times varied from 11 minutes for the small blocks of manganese oil hardening steel to 20 to 25 minutes for the larger cubes of the same grade and all pieces of the other steels.

Hardening temperatures were 1425 degrees Fahr. (775 degrees Cent.) for the manganese oil hardening steel, 1500 degrees Fahr. (815 degrees Cent.) for the 3 per cent manganese air hardening, and 1775 degrees Fahr. (970 degrees Cent.) for the 5 per cent chromium-1 per cent molybdenum steel. Samples after hardening were drawn at 350 degrees Fahr. (190 degrees Cent.)

Measurements after hardening and drawing were made with carefully checked micrometer calipers by two men until agreement

Table III

Effect of Heat Treatment Soaking Time on Manganese Steels

Values represent change in inches from original 2-inch length. Minus sign (—) means shrinkage to less than original length. Numbers in italics are Rockwell C values and magnetic saturation in gausses. Drawn 1 hour at 375 degrees Fahr. (190 degrees Cent.).

Type	Hardened from °F.	°C.	Time at Hardening Temperature — 5 Minutes: Hardened	5 Minutes: Drawn	15 Minutes: Hardened	15 Minutes: Drawn	60 Minutes: Hardened	60 Minutes: Drawn
	1450	790	.0010 *61-62* *10,900*	.0006 *59-59½* *11,600*	.....	.....	.0006 *63* *10,500*	—.0002 *59½-60* *10,750*
3 Mn-1 Cr-1 Mo (tube-cooled)	1500	815	.0008 *63* *10,200*	.0002 *60* *10,700*	.0002 *63* *9,400*	—.0010 *59½-60* *9,700*	—.0002 *63-64* *9,100*	—.0015 *59½-60* *9,400*
	1550	845	.0001 *63-63½* *8,850*	—.0008 *60* *9,300*	—.0010 *62-63* *7,900*	—.0021 *59-60* *8,150*	—.0034 *61-62* *6,800*	—.0048 *58-59* *6,900*
	1500	815	.0018 *62-62½* *12,000*	.0014 *60-60½* *12,400*	.....	.....	.....	.....
2 Mn-2 Cr-1 Mo (tube-cooled)	1550	845	.0021 *62½* *11,650*	.0014 *60-60½* *11,950*	.0019 *62½-63* *11,150*	.0010 *60½* *11,600*	.0011 *63½-64* *10,800*	.0002 *61* *11,050*
	1600	870	.0020 *64½* *10,900*	.0010 *61* *11,400*	.....	.....	.0008 *64½-65* *9,800*	—.0009 *61-61½* *10,100*
	1500	815	.0022 *62-63* *11,750*	.0015 *60½* *12,100*	.....	.....	.....	.....
2 Mn-1 Cr-1 Mo (tube-cooled)	1550	845	.0023 *64-64½* *11,050*	.0012 *61-61½* *11,350*	.0017 *64-64½* *10,000*	.0002 *61* *10,350*	.0005 *64* *9,400*	—.0011 *61* *9,600*
	1600	870	.0017 *64* *9,500*	.0001 *61* *9,800*	.....	.....	—.0018 *61½-62* *7,800*	—.0038 *58-59* *7,900*
	1375	745	.0026 *64* *14,400*	.0013 *61* *14,800*	.0027 *64-65* *13,900*	.0012 *60-61* *14,200*	.0029 *65-65½* *13,500*	.0009 *61-61½* *13,750*
Mn Oil Hardening (oil-quenched)	1425	775	.0030 *65-65½* *13,400*	.0011 *61* *13,900*	.0024 *65* *12,750*	.0006 *61* *13,200*	.0027 *65* *12,400*	.0005 *61-62* *12,800*

Table IV

Effect of Heat Treatment Soaking Time on 5 Cr-1 Mo and High Carbon—High Chromium Types

Values represent change in inches from original 2-inch length. Minus sign (—) means shrinkage to less than original length. Numbers in italics are Rockwell C values and magnetic saturations in gausses. Drawn 1 hour at 375 degrees Fahr. (190 degrees Cent.).

Type	Hardened from °F.	°C.	Time at Hardening Temperature: 5 Minutes Hardened	5 Minutes Drawn	15 Minutes Hardened	15 Minutes Drawn	60 Minutes Hardened	60 Minutes Drawn
	1675	915	.0020 *59-61* *11,850*	.0021 *58-60* *12,700*	.....	.....	.0026 *63½-65* *11,450*	.0019 *62* *11,750*
5 Cr-1 Mo (tube-cooled)	1750	955	.0029 (a) *65-66* *11,400*	.0018 *62½-63* *11,650*	.....	.....	.0029 *65* *9,650*	.0016 *62* *10,050*
	1825	995	.0022 *64-65½* *9,050*	.0007 *61-62½* *9,500*	.....	.....	.0019 *62-64* *7,600*	.0005 *60-62* *7,900*
	1750	955	.0020 *57-61* *11,550*	.0016 *55-58* *11,800*	.....	.....	.0030 *64-65* *10,600*	.0021 *60-61½* *10,900*
2C-12Cr-1V (oil-quenched)	1825	995	.0035 (a) *64½-66* *10,200*	.0024 *61-62½* *10,400*	.0036 *65-66½* *9,900*	.0024 *61-62½* *10,200*	.0038 *66* *9,500*	.0025 *62-63½* *9,750*
	1900	1040	.0038 *65* *8,800*	.0021 *62* *9,050*	.....	.....	.0030 *65-66* *7,750*	.0015 *63* *7,950*
	1750	955	.0005 *55-57* *11,250*	.0007 *54-56* *11,850*	.....	.....	.0015 *61* *11,200*	.0011 *59-60* *11,500*
1.5Cr-12Cr-.7Mo (tube-cooled)	1825	995	.0011 (a) *62½-63* *10,400*	.0004 *59½-61* *10,800*	.0014 *63½-64* *10,100*	.0007 *61-61½* *10,450*	.0014 *63½-65* *10,150*	.0006 *61-62* *10,400*
	1900	1040	.0015 *65* *9,100*	.0004 *61½-62* *9,450*	.....	.....	.0008 *64-64½* *8,000*	.0000 *62* *8,200*

(a) Data from later tests instead of original 5-minute treatment.

was reached. The tendency of the block faces to bulge made use of the Electrolimit gage impractical.

Rockwell readings were made directly on the surface, without any grinding or polishing except a superficial rubbing.

Results

Since the four samples from each group with similar orientations gave quite closely agreeing results, only the average value for each set is reported here. It was necessary to report both maximum and minimum movements, since in some cases the tendency of the sides to swell outwardly at the center made a simple average rather misleading.

Table V presents the averages, on blocks oriented as shown in the accompanying Fig. 5. In each group the value representing the least change among the three types of steel is shown in bold-face type.

It is immediately evident that the 3 per cent manganese air hardening steel has undergone the least dimensional change. The only lower values for any of the tests occurred as minimum change figures in the oil hardening manganese steel; but these few low results are meaningless, since the maximum distortions on the same faces were large. This wide variation in readings corresponds to pronounced swelling or bulging out of the cube faces. The air hardening steels showed this tendency only to a very slight extent.

The influence of grain direction appears to vary with the individual steels. It was apparently least pronounced in the oil hardening steel. For all faces of the cube (shape 3) the values were very similar, while both the other shapes expanded most between the large, square faces, which were in one case with and in the other case across the grain.

The 5 per cent chromium-1 per cent molybdenum steel appeared to expand most in that direction which corresponded to the grain axis. This was true of all three shapes, and the magnitude of the movement was about the same for each. The directions normal to the grain showed very little movement and notably slight tendency to bulge. This is contrary to the observations of Scott and Gray.[3]

The 3 per cent manganese air hardening steel, in contrast, shrank along the grain axis, without, however, showing as much tendency to go out of flatness as the other air hardening steel. In

[3]Howard Scott and T. H. Gray, "Dimensional Changes on Hardening High Chromium Tool Steels," Transactions, American Society for Metals, Vol. 29, 1941, p. 514.

directions normal to the grain its maximum average change in no instance exceeded 0.0006 inch, which in a 2-inch length is a very small distortion.

The user of these three different steels would have to take these individual idiosyncrasies into account when figuring grinding allowances on dies and related parts. Thus, the marked bulging found in the oil hardening steel would necessitate only slight excess of stock before hardening to take care of possible decrease in distances across corners, but plenty of stock would have to be removed after hardening. Pieces of 5 per cent chromium-1 per cent molyb-

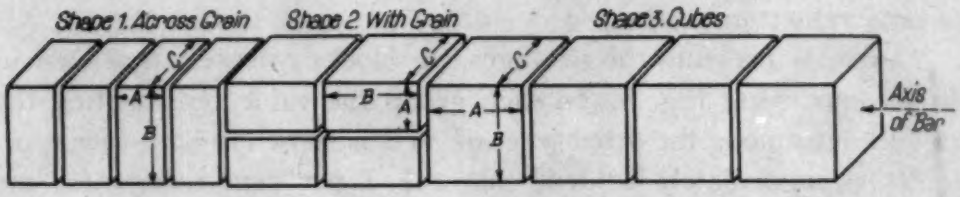


Fig. 5—Orientation of Blocks in Original Bar. Before Heat Treatment, A = 1.005 or 2.005 Inch, B and C = 2.005 Inch.

Table V

Dimensional changes in hardened and drawn blocks. Values represent expansion in inches over original dimensions, except that those preceded by a minus sign (—) represent shrinkage.

	A		B		C		Rockwell C
	Min.	Max.	Min.	Max.	Min.	Max.	As Drawn
Shape (1). Across Grain.							
Oil Hardening Mn	**0.0000**	0.0034	0.0004	0.0020	0.0004	0.0021	59 -59½
5 Per Cent Cr-1 Per Cent Mo	0.0016	0.0022	0.0005	0.0006	0.0006	0.0007	59 -60½
Air Hardening 3 Per Cent Mn	—0.0004	**—0.0006**	**0.0001**	**0.0004**	**—0.0001**	**0.0006**	59 -60
Shape (2). With Grain.							
Oil Hardening Mn	**0.0002**	0.0041	**—0.0001**	0.0014	0.0003	0.0019	58 -59½
5 Per Cent Cr-1 Per Cent Mo	0.0007	0.0008	0.0019	0.0027	0.0005	0.0008	59 -60
Air Hardening 3 Per Cent Mn	**0.0002**	**0.0004**	—0.0007	**—0.0011**	**—0.0001**	**0.0004**	59 -60
Shape (3). Cube.							
Oil Hardening Mn	0.0012	0.0019	0.0013	0.0024	0.0011	0.0020	59 -59½
5 Per Cent Cr-1 Per Cent Mo	0.0019	0.0024	0.0007	0.0010	0.0006	0.0009	59 -60
Air Hardening 3 Per Cent Mn	**—0.0011**	**—0.0015**	**0.0003**	**0.0005**	**0.0001**	**0.0004**	58½-59

denum steel might be made very close to size normal to the grain but scant along the grain, while with the 3 per cent manganese air hardening steel some fullness would have to be allowed along the grain.

This effect of grain undoubtedly influences the linear expansion studies in the first part of this paper, in that only expansion along the grain was measured; but cross-grain samples would have been very difficult and expensive to prepare, besides being much less

uniform. It is felt that the data on blocks sufficiently supplement the linear data to make it useful.

Remarks

The test results reported in this paper must not by any means be construed as an effort to show to a disadvantage any of the steels which were studied. While it would appear that several steels are better from a dimensional change viewpoint than the familiar manganese oil hardening die steel, yet certain very important merits of this analysis must be remembered. Among these are its ease of machining, high hardness, low hardening temperature, and universal availability. The many years it has continued in popularity prove that in the hands of those who know its behavior, it is a very valuable steel.

When extremely low distortion in hardening is desired, then a steel of the air hardening manganese-chromium-molybdenum type has pronounced merit.

Compression tests show that, at the same hardnesses, practically no difference exists between the oil and air hardening types and the 5 per cent chromium-1 per cent molybdenum steel; at about 61 Rockwell C, all have ultimate compressive strengths in the vicinity of 400,000 pounds per square inch.

Service records obtained to date show these three types, the oil hardening and air hardening manganese steels and the chromium-molybdenum steel, to be practically alike in wear resistance, although all are much inferior in that respect to the more expensive high carbon-high chromium types.

Summary and Conclusions

Short rods of various popular die steels were studied for length, magnetic saturation, and hardness changes after heat treatment at various temperatures, then after tempering either at 375 degrees Fahr. (190 degrees Cent.) or at a series of ascending temperatures. Small blocks of three of these steels were also treated according to preferred practice and studied for distortion.

The steel showing the least length change after hardening and shrinkage after tempering was found to be the 3 per cent manganese-1 per cent chromium-1 per cent molybdenum air hardening type.

When hardened from about 1500 degrees Fahr. (815 degrees Cent.), this steel showed very little expansion as hardened and practically none as drawn. The 2 per cent manganese-2 per cent chromium-1 per cent molybdenum and 2 per cent manganese-1 per cent chromium-1 per cent molybdenum types showed slightly more expansion; but after hardening at temperatures somewhat higher than that necessary for the 3 per cent manganese steel they returned to their original length as drawn.

The popular 5 per cent chromium-1 per cent molybdenum steel was not the equal of the manganese air hardening steels as regards length increase, although in the block tests it expanded only very slightly more than the 3 per cent manganese air hardening steel. Differing analyses of the two examples studied showed clearly the strong effect of increasing concentrations of carbide-forming elements in reducing amount of retained austenite and hence increasing expansion.

More prone to expansion than either of these air hardening types was the oil hardening manganese type. Blocks made of it bulged somewhat during treatment, and length changes in rods were greater than either of the other steels, though rods came back almost to their original length after drawing.

Of the high carbon-high chromium types, the air hardening 1½ per cent carbon type was very good as regards length changes, while the 2 per cent carbon oil hardening type expanded about as greatly as any steel studied.

Degree of austenite retention was shown to be the controlling factor in the relative length changes of the air hardening steels; as more austenite was retained, expansion after hardening became less, until with enough retained austenite, actual shrinkage took place. Magnetic saturation measurements correlated well with expansion determinations and are assumed to indicate amount of retained austenite; on that basis, about 30 per cent retained austenite is necessary for minimum length change.

Raising the hardening temperature and lengthening the time at temperature, by causing retention of more austenite, was shown to result in less expansion in the steels whose nature is such as to permit of sufficient of such retention. Only in the case of the manganese air hardening steels, however, is this phenomenon of great practical importance, as the other steels tested require rather high treatment tem-

perature to retain enough austenite to yield no dimensional change.

Austenite remaining after hardening was shown to transform rapidly at drawing temperature above 425 degrees Fahr. (220 degrees Cent.) with accompanying sharp length increases and lower toughness. The greater the amount of austenite, the greater was this expansion.

Oil quenching was shown not to retain significantly more austenite than air cooling, at least in small sections, in those steels capable of air hardening. It did, however, result in greater length changes. No real advantages appeared to be gained by oil quenching such steels, other than slightly lower hardening temperatures and slightly higher hardness.

Acknowledgment

The author wishes to express his appreciation to the officials of the Allegheny Ludlum Steel Corporation for permission to publish this study, which was conducted in its laboratories.

DISCUSSION

Written Discussion: By John E. Erb, Works Laboratory, General Electric Co., Schenectady, N. Y.

This paper by Mr. Butler may be read with profit by all who deal with hardened steels.

For example, it serves to emphasize some very important questions too often disregarded:

1. While hardening to obtain minimum volume changes, what becomes of the hardness, strength, wear resistance, etc.?
2. What is the directional effect?
3. How does varying size or "mass" affect the results with different steels?
4. Ditto with respect to shape?

These questions have been dealt with, on the whole, quite creditably.

We hardly concede, however, as it is implied on page 218, that the user will be able to "figure" grinding allowances unless there is available to him much more data than has yet been published.

Nor is it necessary that this should be so. One of the principal objectives, in the original design of an air hardening nondeforming die steel, was to eliminate grinding after hardening altogether. This objective has, in large measure, been attained.

In conclusion, therefore, it is specially gratifying to the undersigned to be invited to discuss this paper, and to note the high quality as well as the amount of research which is being conducted upon the air hardening steels.

It is even more satisfying to know that they are playing their part in today's industry.

Oral Discussion

W. E. MAHIN:[4] This paper dealt with a subject very interesting from viewpoints both of theory and practice. Low distortion obtained during heat treatment of dies is extremely valuable but it would be interesting to know whether the retained austenite accompanying low distortion has been found by the author to reduce die life. The speaker has had some experience with tests designed to measure die life and it has been his experience that best die life is obtained only with maximum hardness, i.e., about 65 Rockwell C. This hardness apparently would preclude the presence of an appreciable amount of retained austenite.

A. E. BELLIS:[5] This may not be particularly pertinent, but I am rather interested in the availability of this material. I am bringing it up as a possible useful consideration. I notice that manganese and molybdenum are the important ingredients of the steels mentioned. I heard one paper on Monday in which we were told there was going to be a very plentiful supply of manganese, and another one that there was a good supply of molybdenum, and at an evening session it was mentioned that it was in order to buy new equipment so as not to use manganese, but I think that all of us want all the information we can get about the availability of these materials.

I think the author of the present paper might be in a position to tell us whether or not this material will be available, and what other uses it can be put to if we cannot get other tool steels with different alloying elements.

Author's Reply

First of all, I wish to thank Mr. Erb for his favorable comments. I agree that grinding allowances cannot yet be quantitatively evaluated for all the shapes and sizes used in industry. As he mentions, however, the new air hardening nondeforming steels often require little or no grinding after proper hardening.

We do not yet have any really good die life data available to answer Mr. Mahin's question about the relation between die life and hardness. The test pieces we studied were drawn to 60 Rockwell C merely because we were led to believe that this was general practice with users of such steels. Mr. Mahin's value of 65 Rockwell C for best die life seems rather high for applications in which toughness is important; certainly it is a higher hardness than obtainable in any but small sections of the manganese air hardening steels even with no tempering. However, the indications are that at the same degree of hardness, the new manganese air hardening steels are about equal in performance to the oil hardening manganese and the 5 per cent chromium-1 per cent molybdenum

---

[4]Metallurgical engineer, Feeder Engineering Department, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

[5]President, Bellis Heat Treating Co., Branford, Conn.

steels. While the new steels may not develop quite as great hardness in the fully hardened state, yet I am of the opinion that their greater toughness and lessened internal strain (arising from low hardening temperature and relatively slow cooling) might permit lower tempering temperatures. The resulting higher hardness should improve die life, as Mr. Mahin suggests.

Mr. Bellis's inquiry concerning the availability of these new manganese-bearing nondeforming steels can be answered only by the observations that the tonnage of manganese apt to go into these steels is very small compared to that demanded by other ferrous products, and the available supply of that important element would not be significantly decreased even if the new steel entirely replaced the other types of nondeforming steels with relatively low hardening temperatures. Indeed, such replacement might mean a worthwhile saving in chromium. The new steels can, of course, be supplied only under suitable priority ratings.

The uses of this new type of steel have not yet been fully explored. It has been used with outstanding success in the manufacture of various precision gages and other parts in which its exceptional nondeforming quality was valuable. From experience to date, we should not hesitate to recommend this new steel for any application in which the manganese oil hardening or the chromium-molybdenum types have been successful.

I might supplement the data presented in the paper itself by mentioning some later work. From a 4-inch square billet of 3 per cent manganese air hardening steel (steel H, page 192) expansion test pieces 2 by ¼-inch round, as used before, were cut both parallel and perpendicular to the axis of the billet, in positions ranging from the extreme outer edge to the center. These pieces were held 1 hour at 1450 degrees Fahr. (790 degrees Cent.) and cooled in the tube, then drawn at 375 degrees Fahr. (190 degrees Cent.) to give hardness of 60 Rockwell C.

It was interesting to observe that those samples which were cut parallel to the axis of the billet returned very nearly (± 0.0002 inch) to their original lengths after hardening and drawing. However, the samples which were originally perpendicular to the billet axis increased considerably in length, from 0.0006 inch increase near the outer surface of the billet to 0.0017 inch across its center.

From the same billet a chunk 2 inches long by 4 inches square was cut and carefully ground and measured, then hardened in still air after heating a total of 9 hours packed in spent carburizing compound in a furnace at 1450 degrees Fahr. (790 degrees Cent.). It was then drawn for 3 hours at 375 degrees Fahr. (190 degrees Cent.) to a hardness of 59½ Rockwell C.

Along the grain axis (the 2-inch dimension), from 0.0004 to 0.0008 inch expansion resulted, while across the faces 4 inches apart (the billet sides) from 0.0012 to 0.0015 inch expansion was found. When reduced to terms of change per inch, this fails to agree with the behavior of the small samples, in that the expansion of the block along the grain axis was slightly greater than across the grain. The differences are, however, small, and the heat treatment of the block could not be done with as much precision as that of

the small samples. Since the greatest change from the original dimensions did not exceed one and one-half thousandths of an inch in four inches, it is evident that this steel has very little tendency to distort in heat treatment.

HARDENABILITY TESTING OF LOW CARBON STEELS

By R. C. Frerichs and E. S. Rowland

Abstract

Herein are presented the results of hardenability tests performed on four popular grades of low carbon alloy carburizing steels by six different methods. The methods comprise quenching various sizes of cylinders, the end quench test in its various modifications, the so-called "bomb" type of test and the quenching of solid tapered specimens. An attempt has been made to evaluate the six methods from the practical standpoints of adequacy over the range of hardenability of low carbon steels, ease of manipulation and accuracy of results.

Introduction

HARDENABILITY, both in its theoretical aspects and from the standpoint of practical testing, has been the subject of much experimental work and discussion in recent years. Many methods have been proposed for testing hardenability of steels and much thought has been given to the interpretation of results obtained by these methods.

A review of the literature on hardenability and its testing reveals the fact that little work has been published on the hardenability of the low carbon carburizing grades of carbon and alloy steels. This is rather surprising in view of the large tonnage of such steel produced and the close control maintained over core properties for many heavy duty applications.

It is a well known fact that as the hardenability decreases, the problems to be faced in obtaining accurate hardenability data increase enormously. The use of a method of testing which is relatively insensitive to small changes in hardenability and variations in procedure which would have no apparent effect in the case of high hardenability steels may so affect the final result that serious discrepancies appear. For example, it is the opinion of the authors

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. Of the authors, E. S. Rowland is research metallurgist, and R. C. Frerichs is a member of the metallurgical department of the Steel and Tube Division, The Timken Roller Bearing Company, Canton, Ohio. Manuscript received June 23, 1941.

that, in general, oil cannot be used as a quenching medium in the hardenability testing of carburizing steels with satisfactory results because of too low a quenching speed. This statement is made in spite of the fact that the alloy carburizing steels are almost universally oil-quenched in production. The use of water quenching in testing and oil quenching in production hardening of a particular steel is no inconvenience because the fundamentals of hardenability are now sufficiently well understood that correlation can readily be effected between test and production conditions.

The most obvious method of obtaining information regarding the depth of hardness is to prepare a specimen of simple shape, such as a cylinder, quench it in a suitable medium and determine the depth of hardness penetration by measurement on a fractured cross section, a ground and etched section or by hardness measurement at various depths below the surface. This method of testing is widely used and the interpretation of the results obtained has been thoroughly discussed by Grossmann and his associates (1), (2),[1] Queneau and Mayo (3) and by Burns, Moore and Archer (4). Of these interpretive methods, the one proposed by Grossmann is probably the most advantageous from all standpoints and is the one used in the present paper.

It was early recognized that the cylinder test was less accurate on low carbon than on the higher carbon grades of both carbon and alloy steels due to the shallow hardening properties of the former type. Boegehold and Jominy (5) were the first to introduce a test designed specifically for low carbon steels. This test has become well known and involves end quenching a carburized cylinder and measuring the case hardness in a longitudinal direction just under the surface. An adaptation of this test for steels in the uncarburized condition has been described by Jominy (6) and further data in regard to its use have been published by Williams (7).

The cylinder and uncarburized end quench tests are less satisfactory for low than for high hardenability steels due to the fact that during quenching the rate of cooling falls off very rapidly from the quenched surface inward. The completely and partially hardened areas, therefore, lie very close to the quenched surface and are difficult to measure accurately. Several methods have been successfully used to overcome this condition. The L-Bar end quench test

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

described by Jominy (8) effectively extends the range of high rates of cooling inward from the end of the specimen by incorporating a tapered hole at the quenched end of the bar. A test described by Greene and Post (9) gains much the same effect by using a solid tapered specimen which is quenched by immersion and sectioned longitudinally for measurement. The bomb test introduced by McCleary and Wuerfel (10) arrives at the same end by inserting a small cylindrical specimen in a tapered bomb and sealing the specimen with fusible alloy and a threaded plug. The bomb is quenched by immersion and the specimen removed and hardness readings taken longitudinally along its length. This is one of the two methods available for testing steels which can be obtained only in small sizes. The other is an adaptation of the end quench test first proposed by Boegehold (11) and later described in greater detail by Jominy (12). This test also uses fusible alloy to seal a small specimen into a sleeve with a solid bottom which, when assembled, make up a standard end quench specimen. In all the papers reviewed, about all the actual data on hardenability of the carburizing grades of steel are contained in two papers by Jominy (5), (8) and a small amount published by Williams (7).

The following remarks concerning hardenability and its testing must be construed as applying only to the carburizing grades of steel which are in general distinctly shallow hardening and specifically to the four grades tested.

General Procedure

This paper presents hardenability information gained from testing four carburizing grades of open-hearth S.A.E. steels by six different methods. The steels tested were S.A.E. 4120, 3120, 4620 and 4320. Chemical analyses and grain sizes are given in Table I. The standard McQuaid-Ehn grain size is shown, together with the oxidation grain size after both 1- and 2-hour heating periods at 1500 degrees Fahr. (815 degrees Cent.).

The six types of tests used may be described briefly as follows:

A. Cylinders of several sizes quenched both on tongs and in a submerged spray.

B. The carburized end quench test.

C. The end quench test performed in the uncarburized condition.

D. The "L" Bar end quench test.

Table I
Chemical Analysis and Grain Size of Steels Used

Steel	C	Mn	P	S	Si	Cr	Ni	Mo	McQuaid-Ehn	Grain Size Oxidation at 1 Hour	1500 °F. 2 Hours
3120	0.22	0.50	0.016	0.021	0.23	0.65	1.24	0.03	6/8	6/8	6/8
4120	0.21	0.68	0.016	0.016	0.26	0.68	0.16	0.22	6/8	6/8	6/8
4320	0.20	0.67	0.016	0.016	0.27	0.54	1.75	0.26	6/8	6/8	6/8
4620	0.20	0.61	0.015	0.014	0.29	0.14	1.75	0.26	7/8 (6)	6/8	6/8

E. The "bomb" method.

F. The tapered cylinder test.

Steel was available in all four types in a 2¾-inch round size. Specimen sizes from 1 inch to 2 inches in diameter inclusive were prepared from bars forged ¼ inch oversize, normalized from 1600 degrees Fahr. (870 degrees Cent.) and machined to size. Each bar used was etch tested to be sure neither forging defects nor pattern were present. The small specimens for the bomb test were machined from the quarter sections of 1-inch and the 2¼-inch rounds were taken from the original rolled bars.

A uniform quenching temperature of 1500 degrees Fahr. (815 degrees Cent.) was used on all steels for all types of test except for the carburized end quench tests. While this temperature varies somewhat from general practice for some of the types, it is above the Ac_3 temperature of all of them and it was felt that a considerable advantage was to be gained in comparing results with an identical quenching temperature. Water at 70 degrees Fahr. (20 degrees Cent.) was used as a quenching medium in all cases.

In an effort to control as many external factors as possible, the test specimens were finished with a file and copper plated with a minimum of 0.001-inch plate. During heating for quenching, the tests were packed in small containers with spent carburizing compound to protect the copper plate from oxidation. A thermocouple was placed at the center of the carburizing container to ensure that the specimens always reached the quenching temperature. Experimental evidence indicated that about 1½ hours was required for the center thermocouple to reach 1500 degrees Fahr. (815 degrees Cent.). An additional hour was allowed for thorough soaking after the charge was at temperature.

Two exceptions to the above procedure were necessary in individual types of test. The carburized end quench bars and the

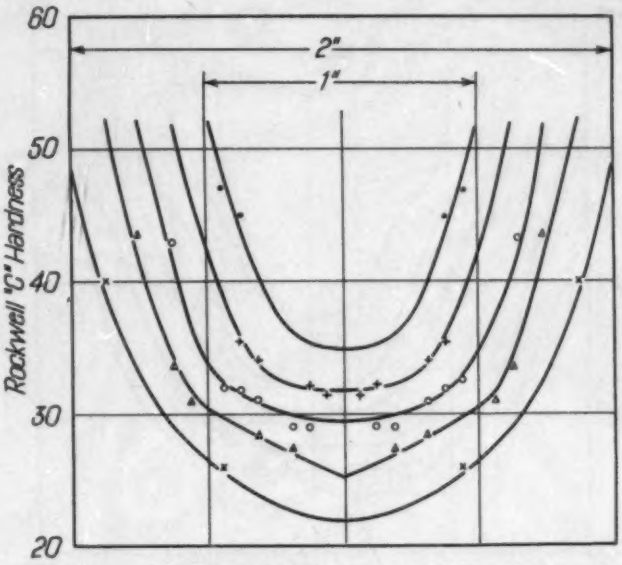


Fig. 1—Hardness Depth Curves of Hand Quenched 4120 Cylinders.

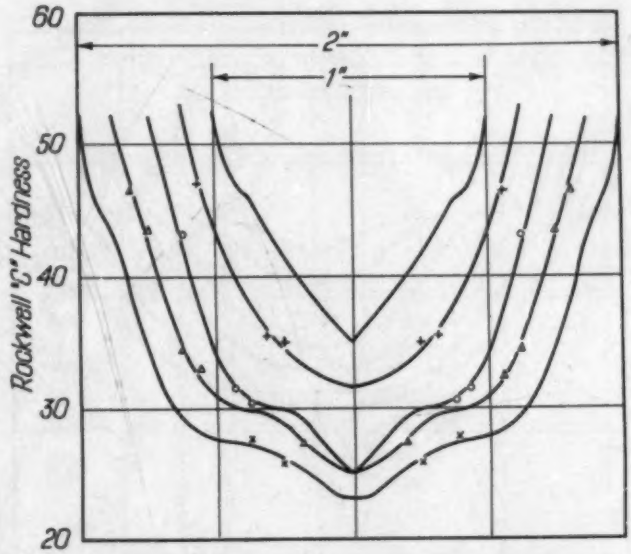


Fig. 2—Hardness Depth Curves of Hand Quenched 3120 Cylinders.

Wuerfel bomb specimens were obviously not copper plated and the latter were heated 1½ hours in an open furnace.

Description of Tests.

A. Cylinder Tests—Duplicate specimens 4½ inches long and 1, 1¼, 1½, 1¾ and 2 inches in diameter were prepared from each type of steel. In addition, 2¼-inch diameter specimens 5 inches long

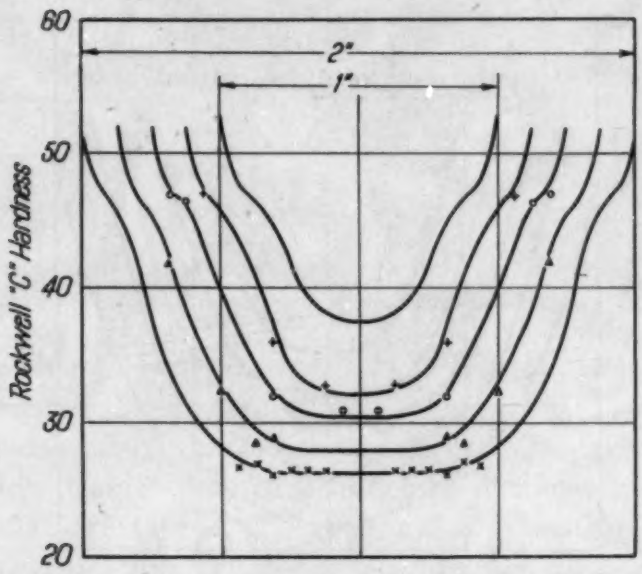


Fig. 3—Hardness Depth Curves of Hand Quenched 4620 Cylinders.

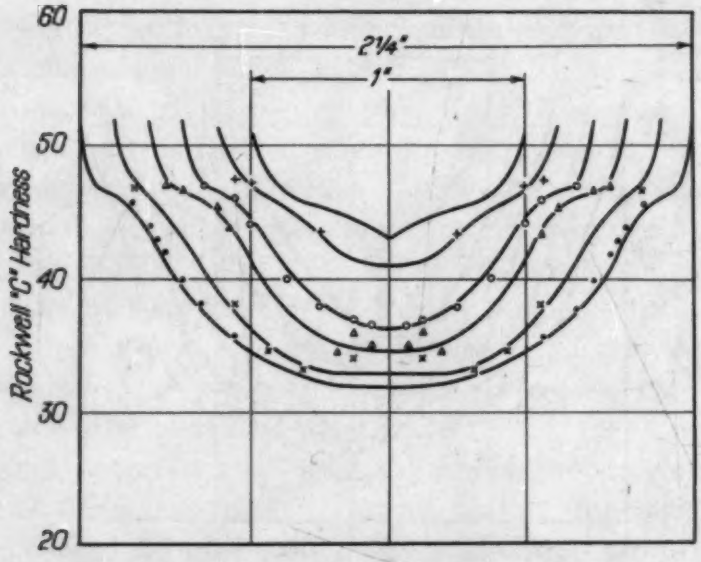


Fig. 4—Hardness Depth Curves of Hand Quenched 4320 Cylinders.

were made from the 4320 steel. All were quenched on tongs in an open water tank, vigorous agitation of the specimen being used to produce as much uniformity as possible. A ½-inch slice was cut transversely from the cylinder with an abrasive water wheel in such a manner that one face was at the exact center of the length after grinding. All ground faces were etched in 2 per cent nital and inspected for temper. Rockwell C hardness readings were taken at

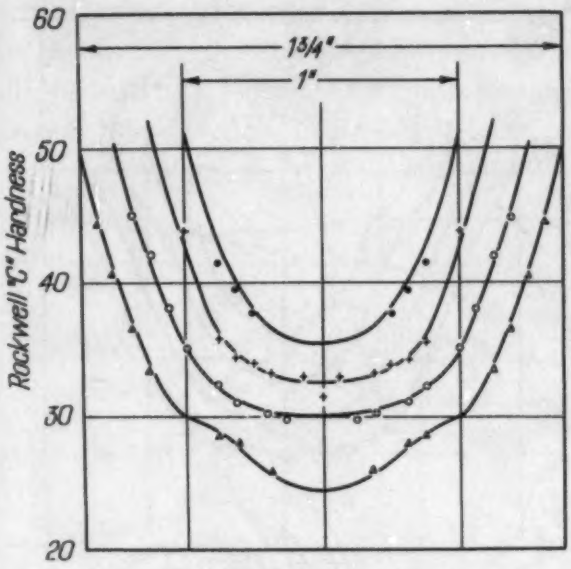


Fig. 5—Hardness Depth Curves of Spray Quenched 4120 Cylinders.

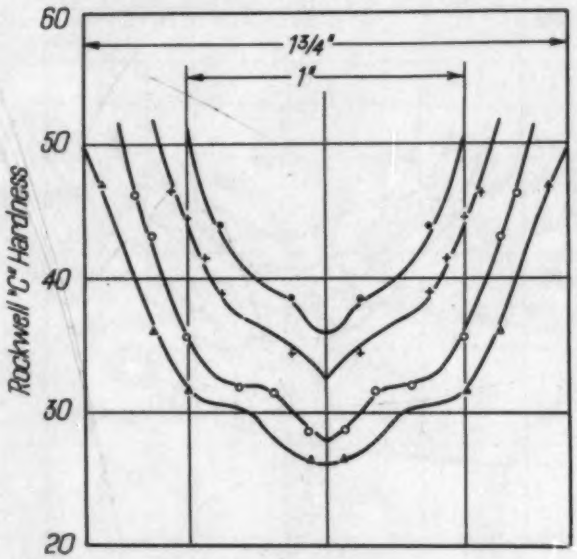


Fig. 6—Hardness Depth Curves of Spray Quenched 3120 Cylinders.

$\frac{1}{16}$-inch intervals on two diameters 90 degrees apart. Surface hardnesses were taken 0.015 inch below the extreme surfaces. All values for each depth were averaged and the resulting data plotted in Figs. 1 through 4. Each point represents the average of eight readings, except for the extreme center points which are an average of only two readings.

The above procedure was duplicated on cylinders which were

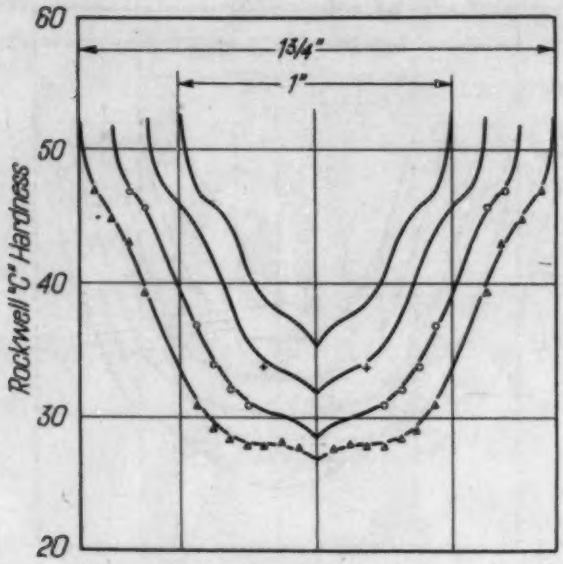


Fig. 7—Hardness Depth Curves of Spray Quenched 4620 Cylinders.

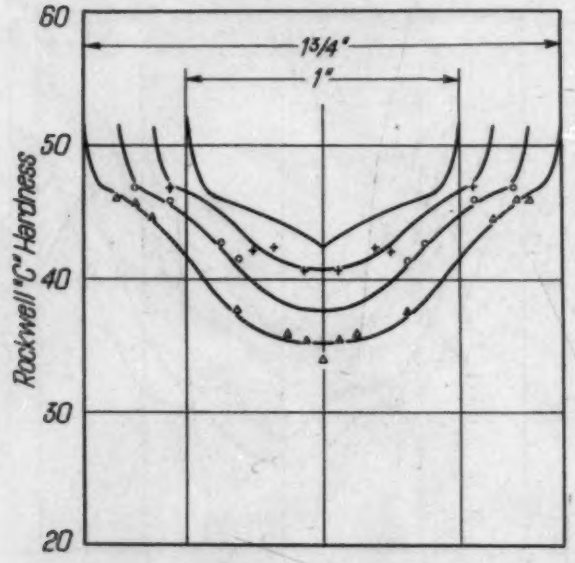


Fig. 8—Hardness Depth Curves of Spray Quenched 4320 Cylinders.

quenched in a submerged water spray. Specimen diameters of 1, 1¼, 1½, and 1¾ inches were used. The spray fixture used consists of a 3-inch I.D. tube, 8 inches long with $\frac{1}{16}$-inch holes drilled on ½-inch centers around the circumference and in rows 1 inch apart. Successive rows of holes are staggered. Water under 30 pounds pressure is pumped through a 1-inch annular space provided around the perforated tube and forced to flow inward through the holes. The fixture

is mounted vertically and submerged in the water tank. The samples are centered in the fixture during quenching. The average data obtained on duplicate tests are plotted in Figs. 5 through 8.

B. Carburized End Quench Tests—Duplicate test specimens of

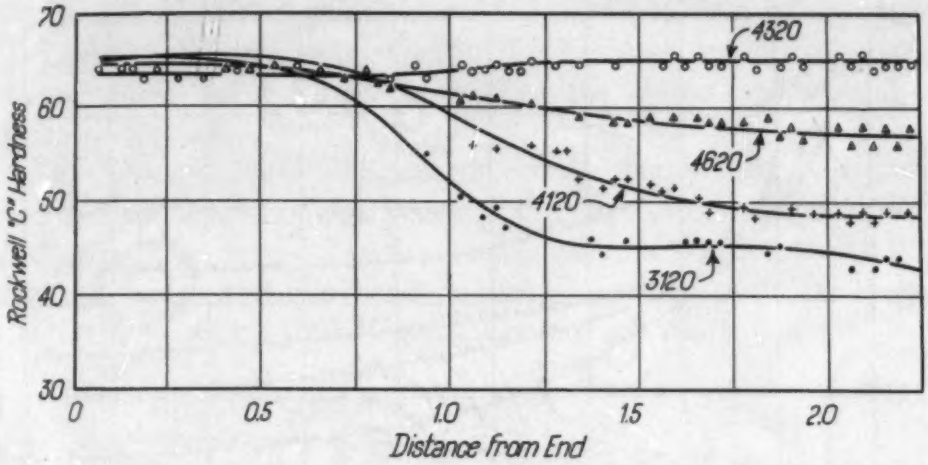


Fig. 9—Hardness Depth Curves Obtained by the Carburized End Quench Method at a Depth of 0.015 Inch Below Surface.

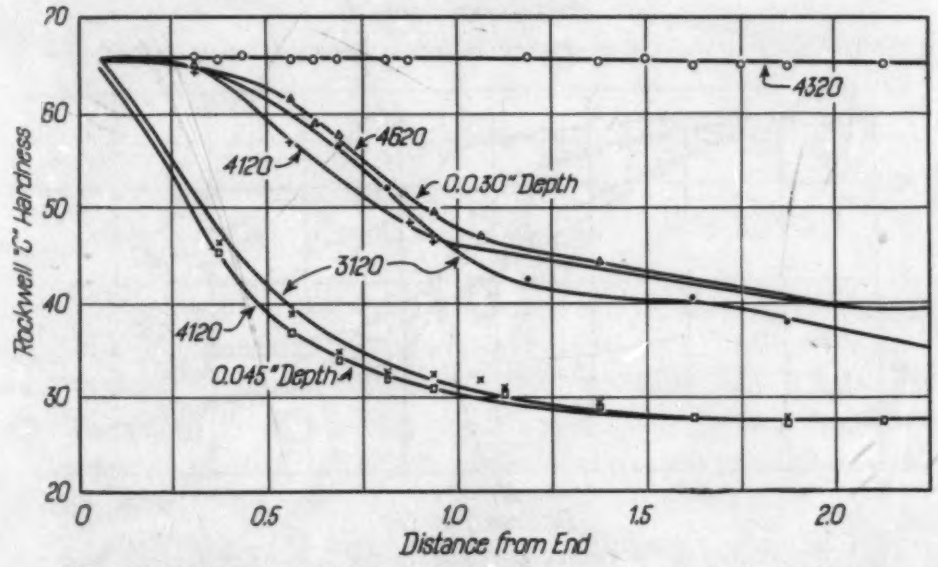


Fig. 10—Hardness Depth Curves Obtained by the Carburized End Quench Method at Depths Below Surface as Indicated.

the four steels, 1-inch in diameter and 3 inches long with a flat end, were heated 8 hours at 1700 degrees Fahr. (925 degrees Cent.) in Rodman carburizing compound with a check thermocouple in the center of the box. The specimens were subsequently cooled on the standard quenching machine in the manner prescribed by Jominy and Boegehold (5). Longitudinal flats were ground on the specimens to

a depth of 0.015 inch at two places 90 degrees apart. Rockwell C hardness readings were taken every $\frac{1}{16}$ inch along the center line of each flat. The readings were started $\frac{1}{16}$ inch from the quenched end on one flat and $\frac{3}{32}$ inch on the other. The hardness values plotted in

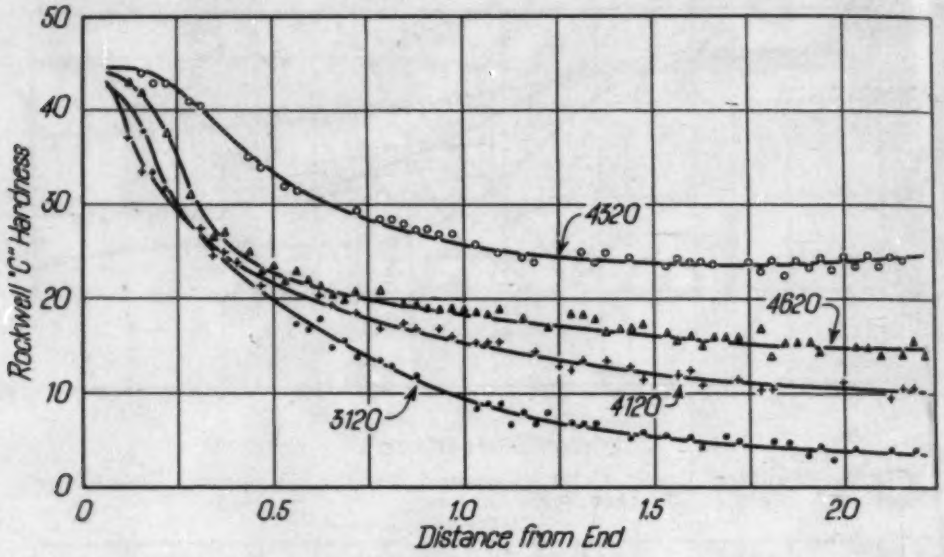


Fig. 11—Hardness Depth Curves Obtained by the Standard End Quench Method.

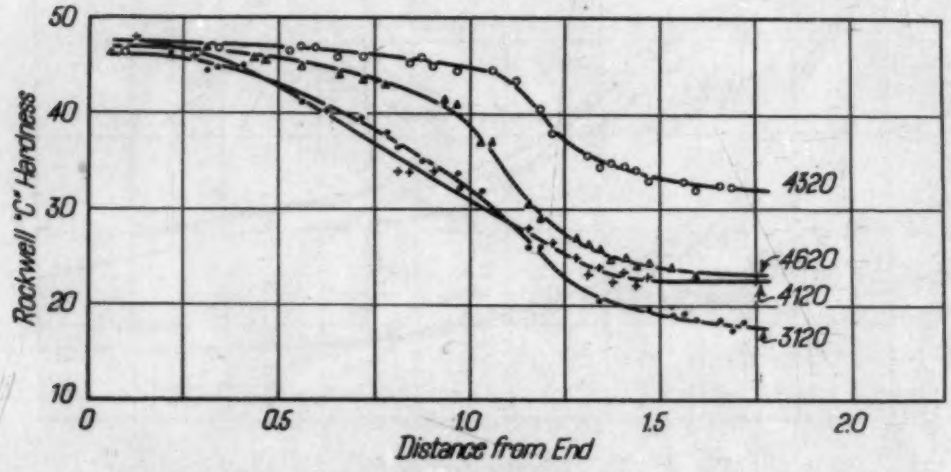


Fig. 12—Hardness Depth Curves Obtained by the L-Bar End Quench Test.

Fig. 9 represent averages of two readings taken every $\frac{1}{32}$ inch after the first $\frac{1}{16}$ inch. The above procedure was repeated on the same specimens but on different flats ground to a depth of 0.030 inch. The average data are plotted in Fig. 10 as are results on 3120 and 4120 steels at a depth of 0.045 inch.

C. Standard End Quench Tests—Duplicate specimens of the four steels and of the same design as were used in the carburized test

were quenched from 1500 degrees Fahr. (815 degrees Cent.) on the same fixture. Average hardness data, obtained on flats of 0.015-inch depth in an identical manner, are plotted in Fig. 11.

D. "L Bar" End Quench Tests—Test specimens, prepared and quenched from 1500 degrees Fahr. (815 degrees Cent.) by the method described by Jominy (8) were run in duplicate on the four steels. The hardness results were obtained in the above manner and are shown in Fig. 12.

E. "Bomb" Tests—The test specimen, bomb and manipulation described by McCleary and Wuerfel (10) were followed in detail in conducting these tests. Duplicate specimens on all four steels, 0.300 inch in diameter and 3 inches long, were quenched in the bomb from 1500 degrees Fahr. (815 degrees Cent.) into the submerged water

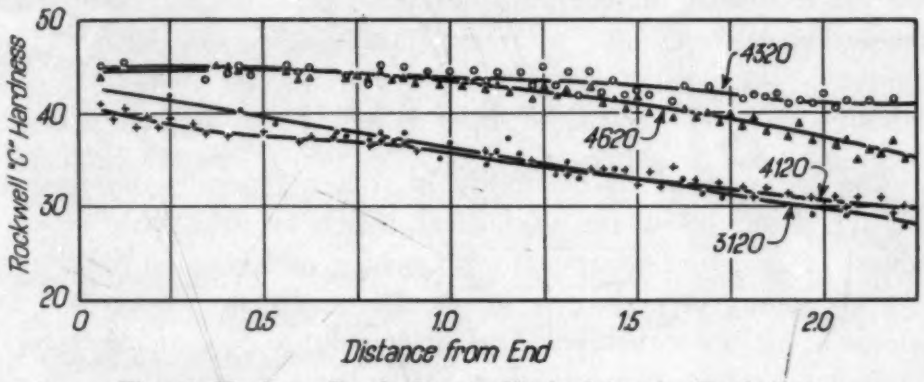


Fig. 13—Hardness Depth Curves Obtained by the Bomb Test.

spray. Rockwell C hardness readings were taken every $\frac{1}{16}$ inch along the length of the specimen and 0.010 inch below the surface on two flats 90 degrees apart. The impressions on the two flats were staggered as on the end quench specimens so that the average hardness data plotted in Fig. 13 represent the average of two readings $\frac{1}{32}$ inch apart.

Taper Tests—The taper test introduced by Greene and Post (9) involves the use of a uniformly tapered specimen ¼ inch in diameter at the small end and 1¼ inches in diameter at the large end. Specimens of all four steels were prepared in duplicate and quenched in the submerged water spray from 1500 degrees Fahr. (815 degrees Cent.). The bars were then cut longitudinally ⅛ inch off the center line on a cut-off wheel and ground to the exact center line of the specimen. All specimens were etched in 2 per cent nital and observed for cutting or grinding temper. A special fixture with a tapered V-shaped

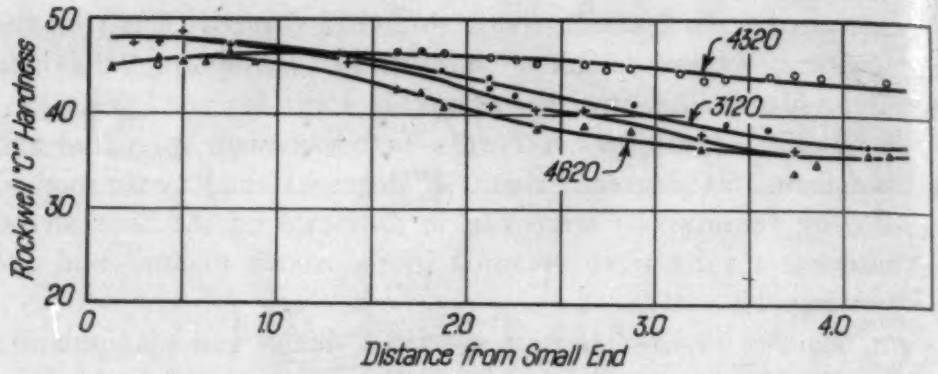


Fig. 14—Hardness Depth Curves Obtained by the Taper Test.

notch was made for the Rockwell machine to correct for the taper of the specimen. Rockwell C hardnesses were taken every ⅛ inch along the length of the bar and the averages of the duplicate specimens plotted in Fig. 14.

Discussion of Results

The criterion of hardenability is rather generally accepted as being the depth below the surface at which an arbitrarily selected hardness or structure occurs after quenching under stated conditions, if the quenching procedure is sufficiently severe to produce a fully martensitic surface structure. Due principally to ease of microscopic estimation, a structure containing 50 per cent martensite is widely used as the measuring stick for depth of hardening. This combination of microconstituents corresponds to a sharp change in color of an etched cross section and, on intermediate and high carbon steels, the depth of hardening can perhaps most accurately be measured by means of a Brinell glass after etching the cross section in boiling 1:1HCl. The 50 per cent martensite structure also corresponds closely to the point of inflection of depth-hardness curves. On medium and high carbon steels, measurement of the depth of hardened fracture produces results which agree quite closely with the 50 per cent martensite point.

On the low carbon steels covered in this paper, however, measurements of etched or fractured sections do not produce sufficiently accurate results and the hardness data must be relied upon for measurement of depth of hardening. The surface hardness of a piece of steel with a fully martensitic structure is recognized as being a function of carbon content alone while the hardness at the 50 per

cent martensite point—the so-called critical hardness—is controlled mainly by carbon content but is also affected somewhat by alloying elements. Microscopic examination of a considerable number of specimens of all four types of steel, on which hardness traverses had been made, led to the conclusion that the critical hardness lay at about 36 to 38 Rockwell C. All estimations in this paper of depth of hardening in the uncarburized condition are based upon a Rockwell hardness of C 37.

A. Cylinder Tests—Both the hand quenched and the spray quenched hardness data on cylinders of various sizes shown in Figs. 1 through 8 were subjected to the hardenability analysis developed by Grossmann and Asimow (1). The H values, critical sizes and ideal critical sizes for each steel under both quenching procedures, calculated from their basic curves, are given in Table II.

In most cases, the plotted points of DU/D versus D fit quite well on one of the characteristic curves published by Grossmann, although a few minor variations were obtained. It is the experience of the authors that a more precise juxtaposition of the experimental data on a single characteristic curve can be obtained with higher carbon steels where hardenability determinations are less sensitive to minor variations in procedure and the depth of hardness can be determined on etched cross sections rather than by hardness determinations as in the present case.

Table II
Ideal Critical Sizes Calculated from Cylinder Tests

	Hand Quench			Spray Quench	
Type	H Value	Critical Size, In.	Ideal Critical Size, In.	H Value	Critical Size, In.	Ideal Critical Size, In.
4120	3.6	0.84	1.10	3.7	0.87	1.16
3120	3.2	0.94	1.23	3.8	1.0	1.22
4620	3.7	1.08	1.34	3.6	1.11	1.37
4320	3.5	1.37	1.61	3.9	1.28	1.54

H values ranging from 3.2 to 3.7 were obtained on a vigorous hand quench and values of 3.6 to 3.9 with the submerged spray. These results are in line with the authors' experience, in that a spray quench is more uniform than a vigorous hand quench but not appreciably a faster quench. The calculated critical sizes agree satisfactorily with the critical sizes estimated from the hardness traverse curves and the calculated ideal critical sizes agree well between the two methods of quenching. More weight should be given to the

hand quenched results since at least four sizes, each larger than the critical size, were available for calculation. The values calculated from Fig. 8 were based on a 42 Rc hardness criterion, since only two sizes of 4320 steel were available at the critical hardness. The theoretical curves of Grossmann do not depend upon any single hardness for a criterion of depth.

Considering the calculated ideal critical size as the measure of hardenability by this method, the four steels tested arrange themselves in order of increasing hardenability as follows: S.A.E. 4120, 3120, 4620 and 4320, with the 4120 and 3120 quite close together. Further perusal of this paper will indicate that all but one other method arranged these steels in the same order. The authors wish to emphasize that this order of hardenability holds only for these four specific heats of steel and does not necessarily represent the order of increasing hardenability for these steel types. This statement is particularly directed at the S.A.E. 3120 and 4120 heats which are so close together in hardenability rating.

B. Carburized End Quench Tests—In their original work on this method, Jominy and Boegehold set as the criterion for hardenability the distance from the quenched end at which the hardness reached 60 Rockwell when measured on a flat 0.015 inch below the surface. They also presented hardness data taken at different depths below the surface which indicated somewhat different characteristics. Table III shows the distances from the quenched end for the various steels at which the hardness reached 60 Rc when measured at different depths below the surface.

Table III

Carburized End Quench Depths at 60 Rockwell C

Type	Distance from Quenched End, Inches		
	0.015 Inch Below Surface	0.030 Inch Below Surface	0.045 Inch Below Surface
4120	0.97	0.485	0.155
3120	0.78	0.56	0.17
4620	1.25	0.61	....
4320	3.0+	3.0+	....

Based upon the results at 0.015 inch depth, the steels arrange themselves in order of increasing hardenability as follows: S.A.E. 3120, 4120, 4620 and 4320. In regard to 3120 and 4120, this is the reverse order of hardenability as compared to that obtained with cylinders. Consequently, hardnesses were obtained at a depth of

0.030 inch on all four steels and the expected order of increasing hardenability obtained, as follows: S.A.E. 4120, 3120, 4620 and 4320. At this depth, however, the hardenability of the 4620 fell back to a value surprisingly close to the 3120. The S.A.E. 4120 and 3120 specimens were later checked at a depth of 0.045 inch and the same order of hardenability maintained. This variation was sufficiently unexpected that an additional set of samples from the 3120 and 4120 steels were prepared, carburized, quenched and new hardness data obtained. The resulting curves lay so close to the ones shown for these two steels in Figs. 9 and 10 that it was decided not to include them.

The above would seem to indicate that the effect of varying carbon content in the high range on steels of different analyses is sufficiently great to disturb the evaluation of some types on this basis. This is only true, of course, when dealing with types which have hardenability ratings close together when evaluated by other methods. The carburized end-quenched method is obviously not well adapted to testing steels which show air hardening characteristics in the carburized condition, of which S.A.E. 4320 is a good example.

C. Standard End Quench Test—The generally accepted criterion of hardenability by this popular method is the distance from the quenched end to the critical hardness. On the basis of an estimated average critical hardness of 37 Rockwell C, the distances to the critical hardness values, taken from Fig. 11, are given in Table IV.

Table IV
Uncarburized Hardenability Ratings by the End Quench Method

Type	Distance to 37 Rc, Inch	
	Standard Bar	L-Bar
4120	0.12	0.72
3120	0.17	0.81
4620	0.22	1.03
4320	0.36	1.25

This method rates the four steels in order of increasing hardenability, as follows: S.A.E. 4120, 3120, 4620 and 4320. The critical hardness falls very close to the quenched end in all but the 4320 steel. The duplicate specimens checked very closely at the critical hardness, however, and it is felt that the results are reasonably accurate. It is desirable to have duplicate hardnesses every $\frac{1}{32}$ inch in the region of the critical hardness for satisfactory estimation of hardenability.

D. "L-Bar" End Quench Test—Using the same measure of

hardenability as on the standard test, the distances from the quenched end to the 37 Rockwell C point are given in Table IV, the values being taken from Fig. 12. The tremendous increase in depth of hardening produced by this test bar over the standard bar considerably improves the sensitivity of the test and increases the experimenter's confidence in the results obtained. The same order of increasing hardenability for the four steels was obtained by both types of hardenability bar.

E. Bomb Test—If the same criterion of hardenability is applied to the results obtained by this method, the distances from the high hardness end to the estimated critical hardness of 37 Rockwell C, given in Table V, again rate the four steels in order of increasing hardenability, as follows: S.A.E. 4120, 3120, 4620 and 4320. With this test method, the hardness-distance curves are spaced farther apart at the critical hardness than by any of the end quench procedures. This is an extremely sensitive test for shallow hardening steels but is not adaptable to the more highly alloyed low carbon steels, such as S.A.E. 4320, without changes in the shape of the bomb.

Table V

Hardenability Ratings by the Bomb and Taper Tests

Type Steel	Distance to 37 Rc, Inch	
	Bomb Test	Taper Test
4120	0.5	3.25
3120	0.81	3.69
4620	2.0	2.88
4320	3.0+	5.0+

F. Taper Test—The distances from the small end of the specimen to the estimated critical hardness for the four steels are given in Table V. In this case, the S.A.E. 4620 steel is rated as the most shallow hardening, followed by S.A.E. 4120, 3120 and 4320. The last named is too highly alloyed an analysis for this test procedure. Inspection of Fig. 7 will show why the 4620 steel has the lowest hardenability rating. The particular bar used for the hand quenched cylinder tests and the taper tests had some negative segregation in the extreme center which radically affected the position of the depth-hardness curve on this test. The evaluation of hardenability by this method would appear to be dependent to a considerable degree upon the amount of center segregation, either positive or negative, in the particular bar tested.

Evaluation of the Hardenability Methods

Table VI is a correlation of the test results based on the order of increasing hardenability when determined by each of the test methods studied. All but the carburized end quench method, when measured at a depth of 0.015 inch below the surface, and the taper test rated the steels in the same order. The same general ratio of hardenability rating was maintained as well. That is, the S.A.E. 4120 and 3120 steels were rated close together, with the S.A.E. 4620 and 4320 much more widely spaced. The carburized test rated them satisfactorily when the hardness was measured 0.030 inch below the surface and the discrepancy in the taper test results is accounted for on the basis of segregation at the extreme center of the 4620 bar used. It can be considered reasonably certain, therefore, that the four heats are rated properly in regard to hardenability characteristics.

It remains to attempt to evaluate the various methods used from the standpoint of their usefulness when applied to carburizing grades of steel. The authors feel that the factors of adequacy over the range of carburizing steels, ease of manipulation of the test including the time consumed in making a large number of tests, and the accuracy of the results obtained are all of importance in evaluating a test method.

Table VI
Steels Arranged in Order of Increasing Hardenability by All Methods

Type Test	Hardenability Criterion	Order of Increasing Hardenability 1	2	3	4
Cylinders	Ideal Critical Size	4120	3120	4620	4320
Carb. End Quench, 0.015-Inch Depth	Distance to 60 Rc	3120	4120	4620	4320
Carb. End Quench, 0.030-Inch Depth	Distance to 60 Rc	4120	3120	4620	4320
Std. End Quench	Distance to Critical Hardness	4120	3120	4620	4320
L-Bar End Quench	Distance to Critical Hardness	4120	3120	4620	4320
Bomb	Distance to Critical Hardness	4120	3120	4620	4320
Taper	Distance to Critical Hardness	4620	4120	3120	4320

The determination of ideal critical size from hardness-depth data on cylinders of various sizes is certainly adequate over the whole range of low carbon carburizing steels if one has available the steel in a sufficiently large size to permit of at least 3 and preferably 4 sizes larger than the critical size or one has accurate information

regarding the H value, in which case only one size larger than the critical size is needed. In making large numbers of tests the time consumed in sectioning and grinding hardened specimens without tempering is a serious problem, particularly when any haste or carelessness will produce misinformation. The authors feel that while the method is more accurate on higher carbon steels where etched cross sections can be used for penetration measurement, it is still sufficiently accurate on low carbon steels for any reasonable purpose. The value of ideal critical size has a certain universal application for determining the hardness penetration in various sizes, shapes and quenching conditions when the quenching conditions are known and controlled. The method has the possible disadvantages of laboriousness in manipulation and the fact that the final answer is indirectly obtained by calculation.

The carburized end quench method is not readily adaptable to steels whose carburized cases are air hardening. From the authors' results, it would appear that the depth below the surface at which the hardness readings are taken has an important bearing on the order in which some different analyses might be rated. The method has the advantage of ease of sample preparation and manipulation as well as reproducibility of results, even when identical samples are carburized at different times.

The standard end quench test is best suited for the higher alloyed and hence the deeper hardening carburizing steels. On the low alloy grades, the critical hardness lies so close to the quenched end of the specimen that any change in the conditions of test may produce an important percentage error in the depth of hardening. The present results indicate that this method is able to differentiate correctly between analyses which are quite close together, but considerable pains are required in the manipulation in order to obtain accurate results. Such factors as scale on the specimen, time from the furnace to the actual quench, etc., are much more important in the case of these low alloy carburizing steels than when dealing with the deeper hardening types. On the other hand, the sample is of a single simple size and shape for a wide range of steels and is easy to prepare, requiring only a drilling and tapping operation. No risky cutting operations are necessary and the small amount of grinding may be done by hand with a minimum of time and equipment. While a special quenching fixture is required, it is quite simple to build and is not beyond the reach of any laboratory.

The L-Bar test specimen is more difficult to make than the standard specimen and it must be accurately prepared since eccentricity of the tapered hole in the end with relation to the O.D. will seriously affect the results. This objection is not too serious, however, since with proper tooling a large number of specimens could be made quickly and accurately at a reasonable cost. The method has all the advantages of the standard test, plus the very important one of considerably increased sensitivity in the low range of hardenability studied. Quite satisfactory reproducibility of results was obtained with this test.

In the hands of a careful and experienced operator the Wuerfel bomb yields perhaps the most precise results of any of the methods studied for steels of low hardenability. The method has extreme sensitivity and will quite readily show measurable differences in hardening power between steels of supposedly identical characteristics when measured by some other methods. The size and taper of the bomb described by the inventors is such that it is not adaptable to the full range of alloy carburizing steels and at least one larger size of bomb would be necessary for testing all such steels. The bomb method is also valuable in the case where steel for testing is available only in small sizes. The manipulation of this test is tedious and more difficult than the others since it requires the use of a fusible alloy with the consequent need for loading and unloading the bomb at a temperature of 200 degrees Fahr. (95 degrees Cent.). It is very important that the fusible alloy "wet" the specimen since, if this fails to occur, the results must be discarded. The bombs are rapidly attacked by the fusible alloy and disintegrate around the plug.

If the slope of the hardness-depth curve is considered as the criterion of sensitivity of a test method, the taper test must be considered as quite sensitive. The specimen is not adapted, in its present size and shape, to testing the higher alloyed carburizing steels. The preparation of the test surface for the hardness determination is quite difficult and time consuming, requiring as it does the longitudinal splitting of a 5-inch length of test specimen. The hardenability rating obtained is always at the mercy of incidental segregation at the extreme center of the bar, a condition which is fairly common in carburizing steels.

Conclusions

It is apparent from the results presented in this paper that the

choice of a method for determining the hardenability of the carburizing grades of steel is dependent upon so many factors that each laboratory must make its own choice. Each method has evident advantages and disadvantages and a choice depends as much on the amount of testing to be done and the speed with which accurate results must be obtained as upon any other factor. If a large amount of testing is required to be done accurately and quickly and samples have to be scheduled through the operating departments, a method is needed which uses a single size of sample for all steels which can be readily prepared and treated and requires a minimum amount of preparation after quenching for accurate hardness testing. Obviously, no one of the above methods entirely fit these requirements and some compromise has to be made. It is the considered opinion of the authors that, when such requirements must be met, a combination of the standard end quench test for the higher alloyed steels and the L-Bar end quench test for the carbon and low alloy carburizing steels represents the best compromise.

If, on the other hand, only a few samples are to be tested periodically and the time consumed is not too important, the choice of a method is almost unlimited. The bomb test is suggested where the ultimate in sensitivity is desired and a careful experimenter is available to perform the tedious manipulation. It is also the authors' opinion that if the carburized end quench test is used, the effect of the depth at which measurements are made should be carefully explored for all analyses tested. It is also considered advisable to make some revision in the taper test which will obviate the necessity of taking hardnesses at the extreme center of the bar.

Bibliography

1. M. A. Grossmann, M. Asimow and S. F. Urban, American Society for Metals Symposium, "Hardenability of Alloy Steels," Oct. 1938, p. 124.
2. M. Asimow and M. A. Grossmann, TRANSACTIONS, American Society for Metals, Vol. 28, 1940, No. 4, p. 949.
3. B. R. Queneau and W. H. Mayo, American Society for Metals Symposium, "Hardenability of Alloy Steels," Oct. 1938, p. 237.
4. J. L. Burns, T. L. Moore and R. S. Archer, TRANSACTIONS, American Society for Metals, Vol. 26, 1938, No. 1, p. 1.
5. W. E. Jominy and A. L. Boegehold, American Society for Metals Symposium, "Carburizing," Oct. 1937, p. 148.
6. W. E. Jominy, American Society for Metals Symposium, "Hardenability of Alloy Steels," Oct. 1938, p. 66.
7. G. T. Williams, TRANSACTIONS, American Society for Metals, Vol. 28, 1940, No. 1, p. 157.

8. W. E. Jominy, TRANSACTIONS, American Society for Metals, Vol. 27, 1939, No. 4, p. 1072.
9. O. V. Greene and C. B. Post, Society of Automotive Engineers, Detroit Meeting, January 1941.
10. F. E. McCleary and R. Wuerfel, Society of Automotive Engineers, Detroit Meeting, January 1941.
11. A. L. Boegehold, Society of Automotive Engineers, Detroit Meeting, January 1941.
12. W. E. Jominy, METAL PROGRESS, Vol. 39, 1941, No. 4, p. 447.

DISCUSSION

Written Discussion: By M. W. Dalrymple, metallurgical supervisor, Bethlehem Steel Co., Bethlehem, Pa.

The conclusion reached by the authors of this paper "Each method (of testing) has evident advantages and disadvantages and a choice depends as much on the amount of testing to be done and the speed with which accurate results must be obtained, as upon any other factor," is one that is gradually gaining the approval of the various investigators of this subject. In other words, no particular test seems capable of satisfying all needs and all individuals.

The truth of this conclusion is confirmed by an experience in attempting to predict the core hardness of a carburized part that is only $\frac{5}{16}$ inch thick. Standard end-quenched and L-bar end-quenched test specimens proved inadequate; and the only method of testing that revealed the core hardness that would be experienced on individual heats, involved the casting of strips of metal ½ inch thick, which were subsequently ground to $\frac{5}{16}$ inch thickness and quenched in the same manner as the finished parts. This method of testing involved no mathematical calculations or interpolations. Results of this test are easily obtainable after the casting of a heat, before it is rolled; and all heats outside the limits of the required hardenability can be diverted to other uses.

The authors' arrangement of the hardenability of the four steels when tested by all methods, as shown in Tables VI, reveals that five of the seven testing methods rated the four grades of steel in the same order of hardenability. This fact emphasizes a method of approach that I feel should underlie the consideration of the relationship between chemical composition and hardenability. I would state this method in these words:

(a) Steel of a given analysis type, has a fairly definite range of hardenability that may be established if samples of a sufficient number of heats are tested under given standardized conditions.

(b) Under these conditions, the hardenability ranges of different analysis types will overlap somewhat; and when the conditions of testing are varied the relative order of hardenability may change.

(c) Taking into account these considerations, however, there still remains a general tendency for the various analysis types to arrange

themselves in a fairly definite order of increasing hardenability that is roughly proportional to the increase in the amount of hardening elements present.

(d) Therefore it appears logical for a consumer, with a hardenability problem, to select a steel of an analysis type that is commensurate with his hardenability needs. Having done this, he should then specify this type of analysis, with a definite hardenability requirement, but without any narrow restrictive specification on the percentages of the various elements permissible.

If this method of approach would be generally agreed upon, I feel that a great deal of the difficulty connected with present day chemical and hardenability specifications would be removed. In the first place, the steel producers would not be handicapped, as they so often are now, in attempting to melt steel to narrow chemical limits that often are not compatible with the desired hardenability. On the other hand, the consumer could more easily and more quickly obtain the type of steel he desires with the required hardenability that he needs for his job.

The choice of testing procedure to be followed in carrying out this suggested method of approach depends, as the authors of this paper state, "....as much on the amount of testing to be done and the speed with which accurate results must be obtained as upon any other factor."

Written Discussion: By W. E. Jominy, metallurgist, engineering department, Chrysler Corp., Detroit.

The evaluation of the methods of testing hardenability presented in this paper is quite well considered. It would be worth while for those who are faced with the necessity of making hardenability tests and concerned as to which test to apply, to carefully read this paper. The authors have shown that the choice of test depends upon the kind of steel to be tested as well as the conditions of application.

I am particularly interested in the results obtained with the carburizing steels in the carburized condition. It is to be expected that the hardenability of the case is quite different from the hardenability of the core, the case having deeper hardenability. However, it has been my experience that the added increase in hardenability due to carburizing is not a constant, except of course for repeated tests on the same steel. For this reason it is easily possible that the order of hardenability of two steels will be different in the case and in the core, which is what the authors of this paper found, as shown in Tables III and IV.

Another point to bear in mind is that these steels will vary from heat to heat. The carburized end-cooled bar of S.A.E. 4620 steel in Table III gives a reading of 1.25 inches at 0.015 inches beneath the surface. I have found with S.A.E. 4620 in the carburized condition that some heats give as low as 0.5 inches and other heats as deep as 3 inches.

The relative order of hardenability will often change as the depth below the surface of the end-cooled bar is varied. Since the carbon content changes from the surface to the core the hardenability at any depth is that of the average carbon content of the steel affected by the Rockwell C indenter. It is

often of interest to know the hardness at the surface before any grinding is done to compare with parts like gears whose teeth will not be ground. With many steels there is a tendency for this surface to be austenitic and definitely softer than at 0.015 or 0.030 below the surface.

Written Discussion: By F. F. Vaughn, assistant chief metallurgist, Caterpillar Tractor Co., Peoria, Ill.

The authors are deserving of compliment for having presented some most helpful comparative hardenability test data and for the practical viewpoint observed in their interpretation of the results obtained with the several test methods used.

In the introduction of their paper, the authors state that the most obvious method of obtaining information regarding the depth of hardness is to prepare a specimen of simple shape, such as a cylinder, quench it in a suitable medium and determine the depth of hardness on a fractured cross section, a ground and etched section or by hardness measurement at various depths below the surface. Reference is made to several papers on the interpretation of results obtained by these methods, including one by Burns, Moore and Archer, in which the area below the hardness penetration curve for a 1-inch round specimen was suggested as an index of hardenability and it was proposed that this area be expressed in terms of "Rockwell Inches".

Although we have used this method for many years for evaluating hardenability of medium carbon steels only, it is of considerable interest to note that a similar adaptation of the hardness penetration data for 1-inch specimens in Figs. 1 to 8 inclusive, yields the following "Rockwell Inch" values:

	Hand Quench		Spray Quench	
Steel	Figure	Rockwell Inches	Figure	Rockwell Inches
S.A.E. 4120	1	40.6	5	39.9
S.A.E. 3120	2	41.6	6	40.9
S.A.E. 4620	3	42.6	7	41.9
S.A.E. 4320	4	45.9	8	45.4

It may be noted that this interpretation of the results obtained by the authors, with the simplest of the methods used, definitely evaluates the steels tested in the same order of increasing hardenability as obtained with the other methods, namely,

Order of Increasing Hardenability

1	2	3	4
S.A.E. 4120	S.A.E. 3120	S.A.E. 4620	S.A.E. 4320

The hardness value Rockwell C-52, indicated as quenched hardness obtained on the surface of several of the specimens in Figs. 1 to 8 inclusive, is somewhat higher than the maximum obtainable hardness reported by several other investigators, and according to our own experience, with steels of 0.20 to 0.22 per cent carbon. It is also considerably higher than the maximum shown by the authors for any of the other type specimens they used. We question this departure from normal expectancy.

Oral Discussion

O. V. GREENE:[1] Very likely some of the discrepancy found in the car-

[1]Assistant metallurgist, Carpenter Steel Co., Reading, Pa.

burized end-quenched specimens may be due to the difficulty in determining the critical hardness. The very soft cores found in the carburizing steels probably make the interpretation of this test difficult.

The Carpenter taper test has also been employed in this work to good advantages. This test was originally devised for very shallow hardening high carbon steels and we have never attempted to use it for the deeper hardening alloy steels. The cone test is extremely sensitive and not particularly useful when made of the deeper hardening steels. We believe that the Jominy end-quench test is probably one of the most useful types to use in the investigation of deep hardening steels.

Authors' Reply

We wish to thank the discussers of this paper for their comments.

We are in agreement with Mr. Dalrymple's remarks concerning hardenability testing in general and that the hardenability requirement is often of more value than a restrictive chemical specification.

We were certainly glad to learn that Mr. Jominy had found the same variation in hardenability between different types at different depths below the surface of the carburized end-quenched bar. It is certain that this test is reproducible on the same steel within quite narrow limits but for interpretive purposes it is necessary to know how different types of steel will perform in this test.

Mr. Vaughn's remarks are certainly appreciated as well as his calculation of the "Rockwell Inch" values for the 1-inch rounds. In regard to the surface hardness on the water-quenched cylinders, the maximum hardness obtained of 51.5 Rockwell C was at least equalled and in most cases exceeded when ⅛-inch thick slices from the same bars were quenched in the same manner but without copper plating or protection in the furnace. All plated specimens were checked microscopically and found to be free from carburization. It has been our experience that the published maximum hardness values are slightly low in the low carbon range.

Mr. Greene's discussion is valued because of the large amount of information he has accumulated on the taper test. We wish to state that we are not in disagreement with him on the value of this test for high carbon low hardenability steels. We were looking for a test to use in our laboratory which would be applicable to low carbon alloy steels and we tried the taper test with the results presented in the paper.